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THE FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

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April, 1946.

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THE FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

A general review of the process, the development of the technique of catalyst testing, and studies of various catalysts.

Submitted in Partial Fulfillment
of the
Requirements for the Degree of
MASTER OF SCIENCE

by

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April,1946

1946
#13

Acknowledgement

The authors wish to take this opportunity to extend sincere thanks to all those who have assisted in this investigation:

To the late Dr. E. H. Boomer, director of the project, whose knowledge and wide experience made this project possible.

To Dr. S. G. Davis, whose guidance and assistance was of great value.

To J. G. Knudsen, for his supervision and untiring assistance.

To the Research Council of Alberta, who financed this project.

To the Consolidated Mining and Smelting Company of Canada for the Cominco Fellowship which was of assistance in carrying out the project.

To the Department of Chemistry for services and supplies.

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INTRODUCTION

In recent years, particularly during World War II, it has become increasingly apparent that the reserves of crude petroleum on this continent, at the present rate of depletion, will be sufficient for only a comparatively short time. The rate of discovery of new fields has not been proportional to the increase in consumption of petroleum products, despite the most intensive oil exploration program in history. In view of these facts, it would appear that new sources of liquid fuel must be sought very shortly if this continent is to remain self-sufficient with respect to these products. The last World War has made this requirement almost a necessity.

Fortunately, a number of processes for the production of synthetic liquid fuels have been developed to the industrial stage, and it may be confidently stated that in the very near future, one or more of these will be able to compete successfully in markets now supplied by crude petroleum. As research work continues, technical advances will doubtless lower the manufacturing price to a figure which is competitive with the corresponding products from petroleum. Indeed, one synthetic gasoline plant is now contemplated on this continent.

The basis of all processes for producing synthetic petroleum depends on the hydrogenation of carbon from some source to form the hydrocarbons desired. The carbon may be supplied by coal, coke, natural gas, or even

agricultural products. The hydrogen may be obtained by utilizing any one of a number of common industrial methods for the manufacture of this gas.

Of the processes existing today there are two which appear decidedly the most attractive. The first, the Bergius process, involves the direct hydrogenation of high-rank bituminous or sub-bituminous coals at elevated temperatures and pressures. The second, the Fischer-Tropsch process, carries out an indirect hydrogenation of carbon by means of the reduction of carbon monoxide at moderate temperatures and pressures. Both of these methods are being intensively investigated at the present time.

The possibility of producing aliphatic hydrocarbons, other than methane, was first shown by the Badische Anilin und Soda-Fabrik A.G. in 1913, and by Fischer and Tropsch in 1923 with the development of the "synthol" process. By this method carbon monoxide was catalytically reduced at high temperatures and pressures to form a mixture of aldehydes, alcohols, fatty acids and hydrocarbons. In succeeding experiments during 1925-26, a product consisting almost entirely of hydrocarbons was obtained by using lower temperatures and pressures and a more active catalyst.

In later years, Fischer and Tropsch further widened the scope of their process by varying the temperatures and pressures, the carbon monoxide-hydrogen ratio of the feed gas, and the type of catalyst. English and American workers also carried out a variety of investigations upon

the same process in the years from 1928-1938. Many types of active catalysts have been developed, and a large number of products have been produced in laboratory tests, with yields up to 85% of the theoretical being obtained by some workers.

In 1933, the first commercial Fischer-Tropsch plant was built by the Ruhrchemie A.G. at Oberhausen, Germany. By 1935 five plants were in operation, and by 1942 a production of 5,590,000 bbls. annually of gasoline, diesel oil, lubricating oil and waxes, (about 1/10 of the total German oil production) had been attained. According to the most recent reports, very little additional progress seems to have been made in Germany during the war years. It should be borne in mind that although Germany produced a good share of its petroleum products by the Fischer-Tropsch and other indirect processes, all such plants were subsidized by the government.

The advantages of the Fischer-Tropsch process may be briefly listed as follows:

1. Almost any kind of solid, liquid or gaseous fuel can be used as a raw material.
2. No costly equipment, difficult to fabricate, or to operate at high pressures, is required.
3. Large plants are not necessary for maximum economy.
4. Lubricating oils and a large number of chemical by-products can be made.

5. The process has great flexibility, and offers wide opportunities for further technical and economic improvements.

Against these advantages is the fact that the gasoline obtained from the Fischer-Tropsch primary product has a low octane number. Diesel and lubricating oils produced, however, are of excellent quality, and by modern refinery methods the octane rating of the gasoline can be raised to a higher value. New variations in this process are also being developed which give a gasoline with more favorable anti-knock properties.

In comparison to the Bergius process of coal hydrogenation, the Fischer-Tropsch process does not require the expensive high pressure equipment, or such large installations for maximum economy. Most authorities estimate a considerably lower cost for gasoline from the Fischer-Tropsch process than that obtained from coal hydrogenation. The Bergius process does, however, yield an excellent grade of gasoline, but the diesel fuels and lubricating oils produced are of a low quality.

The economics of the Fischer-Tropsch process, in a large degree, depend on the costs of producing the synthesis gas. At present, natural gas is by far the cheapest source of the necessary carbon monoxide and hydrogen. However, further technical advances in the gasification of coal, particularly by the European method of continuous gasification, about which little is known, may change the picture greatly.

Probably the widest scope for improvement of the process lies in this field.

The development of cheaper and more active catalysts also offers an important field for advancement. The possibility of employing specific types of catalysts to manufacture any desired hydrocarbon product has also been demonstated by several workers. Progress in these respects will do much to place the Fischer-Tropsch process on a competitive basis.

LITERATURE REVIEW

As the economic possibilities of the Fischer-Tropsch synthesis have increased, the incentive for experimental work has been stimulated, thus increasing the literature on the subject. From the historical background of the process it will have been noted that the main research and development was done by the Germans, English, Americans and Japanese. All phases of the synthesis have been dealt with in voluminous detail.

Much of the literature is available only in the languages of the countries in which the researchers have worked. German discoveries, however, have been considered of such value that full translations of much of the work are available in American Journals. Abstracts (76) and comprehensive reviews (43,68) of research work done in all countries have also been made, so that it is possible to obtain a detailed literature review from documents published in English.

Synthesis Gas

Fischer (24) has told how research on synthesis gas had its beginning in the discovery that uni-carbon molecules could be built from carbon monoxide. Sabatier in 1913 produced methane by the reaction $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$. A nickel catalyst was used. Multicarbon members of the hydrocarbon family were the next to be synthesized from a gas containing the same two constituents. The ratio in which carbon monoxide and hydrogen could be present was not rigidly

fixed, and variations were found to affect the properties of the product. The stoichiometric equation for the production of hydrocarbons calls for one volume of carbon monoxide for every two volumes of hydrogen when using specific catalysts. In practice this ratio is favored, although a mixture with less hydrogen is acceptable for synthesis.

Many writers have acclaimed the versatility of this process of hydrocarbon synthesis because of the great variety of materials which can be made to yield the required mixture of carbon monoxide and hydrogen. Coal, coke, methane or any carbonaceous material can be used.

Underwood (75) has listed seven methods for producing this mixture of these two gases from either coal or coke. The gas produced by any of these methods is deficient in hydrogen content if a $2H_2/1CO$ ratio gas is desired.

It is known that the reaction between steam and compounds of carbon such as coal or coke gives a mixture of carbon monoxide and hydrogen known as water gas, the average composition of this gas being, hydrogen, 50%; carbon monoxide, 40%; carbon dioxide, 5%; nitrogen, 5%. In the older type generators this gas is made by alternating steam and air over the hot carbonaceous material. The air gives the required temperature necessary for the steam blast. Many types of continuous generators are employed today. Gasification of solid fuels will be discussed more thoroughly in a later section. To increase the proportion of hydrogen produced by either noncontinuous or continuous methods the carbon content can be lowered by conversion of carbon monoxide to carbon

dioxide by the water gas shift reaction. This also increases the hydrogen content.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

The Germans were thus able to change the proportions of the above mentioned water gas to a gas having the following composition: hydrogen, 55%; carbon monoxide, 27.5%; carbon dioxide, 14%; methane, 0.6%; nitrogen, 2.7%; oxygen, 0.2%. This 2/1 ratio gas was called synthesis gas.

Fischer has recommended (24) synthesis gas production by passing steam and coal gas over coke in a gas producer. The methane of the coal gas is changed to hydrogen and carbon monoxide in a 3/1 ratio. The coal gas ($H_2/CO=10/1$) contributes the hydrogen necessary to give a product which has a hydrogen to carbon monoxide ratio of 2/1.

Methane is an excellent source of hydrogen-carbon monoxide gas. Berthelot (47) has listed the following reactions as the easiest methods of producing the gas:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ + 50 \text{ Cal.}$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 - 7 \text{ Cal.}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \ + 60 \text{ Cal.}$$

The use of catalysts greatly extends the possibilities of the above reactions. Boomer (6) has pointed out that the second reaction is the only one producing a gas with a proportion of $2H_2/1CO$. A combination of the first and third reactions mentioned above in the correct proportions would also yield the necessary ratio. The exothermic reaction works well and has commercial possibilities if oxygen is available at low cost. (It is now produced at $10.00 per ton by liquification.) It

is claimed that the addition of small amounts of steam to the methane-oxygen mixture improves the conversion without increasing the proportion of hydrogen excessively.

Hawk, Golden, Storch and Fieldner (46) have found that the paraffins above methane in the hydrocarbon series are more easily converted to hydrogen and carbon monoxide than methane is but they break down to carbon and hydrogen more easily.

Petrick (59) has claimed the production of better water gas from wood, straw, starch or any other available carbohydrates. The equation for such a reaction is

$$C_6H_{10}O_5 \rightarrow C + 5CO + 5H_2$$

Synthesis gas must be free from sulfur, oxygen and other catalyst poisons. The greatest difficulty is encountered in removing the sulfur compounds. This is essential since the sulfur is adsorbed on the surface of the catalyst to give conditions which diminish the yields of the product and make regeneration of the catalyst impossible.

With the catalysts now in use, one grain of sulfur per 1,000 cu.ft. of synthesis gas (0.2 grams per 100 cu. meters) is the accepted maximum concentration according to many research workers. Since the sulfur content is usually greater than this, either purification of the synthesis gas or the development of a sulfur resistant catalyst is necessary. The former has been used almost exclusively. A multi-stage process has been recommended by Roelen (68). The first step is the removal of hydrogen sulfide by the use of moist ferric oxide. The second step is the extraction of part of the organic sulfur by decomposition with sulfurized iron and alkali metal carbonate

at temperatures between 300 and 450°C. The process followed in step one is then used to remove this hydrogen sulfide. The last step is the removal of any remaining sulfur by passing the gas over a mixture of iron oxide and alkali metal carbonate at temperatures between 150 and 300°C. Funosaka (41) has claimed the best desulfurization is obtained with an iron-copper-pumice catalyst but adequate removal of sulfur can be obtained by passing the gas over luxmasse activated with 10% nickel or copper hydroxide at temperatures between 200-250°C. An addition of 10% each of sodium hydroxide and thoria improves the latter mixture. To remove organic sulfur Fischer and his associates (34) heated the synthesis gas to 400°C. in the presence of an iron catalyst followed by scrubbing with an alkaline ferricyanide solution.

Myddleton (56) has claimed to have developed a sulfur resistant catalyst which he used with a gas containing 250 grains of organic sulfur per 1,000 cu. ft. of blue water gas ($1H_2/1CO$). The activity of this new catalyst persisted even when enough sulfur had been passed through to convert 25% of the metal into the sulfide (approximately one month). Underwood is doubtful if this catalyst has been run for a sufficient length of time to verify the claims made for it.

Both Japanese and English investigators have reported that small amounts of hydrogen sulfide in the synthesis gas act catalytically to increase the yields of kogasin. (This term is a contraction of the German: Kohle-Gas-Benzine referring to the total product from the synthesis, consisting almost entirely of hydrocarbons ranging

from ethane to solid paraffin.) Herington and Woodward (49) have obtained the following results for cobalt-thoria-Kieselguhr (100:18:100):

Table I

Amount of Sulfur Added milligrams per gram of catalyst	Catalyst Temperature °C	Ratio of Hydrocarbon Yield to Corresponding Yield before Addition of Sulfur	
		Condensed Oil	Hydrocarbons in Off-Gas $n = 1.7$
0.00	183	1.0	1.0
0.67	183	2.3	1.0
3.50	183	2.1	0.8
7.94	183	...	0.5
7.94	195	2.0	1.3
13.4	195	1.5	...
33.5	207	1.2	2.1

The addition of hydrogen sulfide containing more than 8 milligrams of sulfur per gram of catalyst resulted in a continuous decrease in activity. This was offset by a rise in temperature as shown in the table. Amounts of sulfur above the quantities listed reduced the catalyst activity until complete poisoning took place. Since the sulfur content builds up on the catalyst, the upper limit of the values in the table will be reached and exceeded. From this investigation it is apparent that low hydrogen sulfide as well as low total sulfur content is

necessary. This is particularly important since sulfur poisoning is irreversible -- the catalyst cannot be reactivated.

As mentioned above synthesis gas must be free from oxygen as well as sulfur since oxygen also poisons the catalysts. The metal carbide formed on the catalyst surface is very prone to oxidation. Thus activity is destroyed. A high temperature activation (hydrogen flow over the catalyst at 380-400°C.) revivifies the catalyst.

Catalysts

A Fischer-Tropsch catalyst has been defined as one which below ten atmospheres of pressure produces hydrocarbons almost exclusively. As the pressure is increased above ten atmospheres oxygenated compounds are formed. According to Komarewsky and Riesz (52) the functions of a catalyst are: the ability to form a carbide from carbon monoxide, hydrogenating ability and polymerizing ability.

Research workers, at an early date in their investigations, found that the main elements which fulfil the above requirements are in group VIII of the periodic table. To date the only elements of this group which have proved to be suitable are cobalt, nickel, iron and r~~h~~uthenium. Cobalt and nickel are usually grouped together as one type while iron and r~~h~~uthenium are a second and third type respectively. Cobalt, nickel and iron, however, may be grouped together since all workers have found that they are characterized by high sensitivity to temperature and to poisons such as sulfur. Very recently the Germans are reported to have developed catalysts the main element of which lies outside group VIII

of the periodic table.(78)

The available literature indicates that cobalt catalysts behave more favorably than any of the others. According to Underwood (75) in addition to giving the highest yields of hydrocarbons they have the longest life. Cobalt catalysts lose activity slowly when used in the pressure range from 1 atmosphere to 7 atmospheres (6) . For the first six months they must be activated every four to seven days with hydrogen at 10-15°C. above operating temperatures. After this period it is necessary to activate them with hydrogen at 380-400°C.

Fujimura and Tsuneoka (42) found that cobalt catalysts containing five to ten percent copper, four to fifteen percent manganese oxide, four to twelve percent thoria, alumina or uranium oxide mixed with one and one-quarter times their weight of kieselguhr yielded 120-170 cc. of liquid hydrocarbon per cubic meter of synthesis gas in one pass. When equal parts of cobalt and nickel were used, without the addition of thoria or alumina promoters, a very poor catalyst for hydrocarbon synthesis resulted. Workers at the Kaiser Wilhelm Institute, Germany, state that mixtures of nickel and cobalt, with or without promotors and inerts, are not satisfactory (66)

In most of the work done by Fischer and his associates a cobalt-copper-thoria-kieselguhr catalyst has been used. With a cobalt-thoria-kieselguhr catalyst at six atmospheres pressure and a $2H_2/1CO$ mixture of gas a maximum yield of 183 grams per cu. meter was obtained. This is eighty-

eight percent of the theoretical yield of 208 grams per cu. meter (69) . From experimental work on loss of cobalt catalysts due to formation of carbonyls it was found that under 50 atmospheres of pressure, the cobalt catalyst does not form carbonyls. Above 100 atmospheres consumption of the catalyst by vaporization of the carbonyls was noted (25). Very recent information states that cobalt catalysts are the only ones suitable for synthesis at atmospheric pressure (66).

The overall reaction using a cobalt catalyst is written as:

$$9CO + 19H_2 \longrightarrow C_9H_{20} + 9\ H_2O - 267,600 \text{ calories}$$

Nickel catalysts have been used with varying degrees of success. Since the hydrogenation tendency is much greater with nickel than with cobalt a more saturated product results, giving a gasoline fraction with a lower octane number.

Fujimura and Tsunooka (42)found that nickel with 20% manganese oxide and 4-8% of thoria, alumina, tungstic oxide or uranium oxide, along with 1.25 times its weight of kieselguhr, yields 100-160 cc. of liquid hydrocarbon per cubic meter of synthesis gas. The optimum temperature increased from 185 to 210°C.

In reports published by Fischer and his co-workors (22) nickel catalysts using thoria or manganese oxide as a promoter and kieselguhr as a refractory were described. At 200°C. a yield of from 100-153 cc. per cu. meter of synthesis gas was obtained. The precipitation method was claimed as the best preparatory procedure to be followed. Potassium

carbonate was the most effective precipitator. Thirteen percent thoria was the optimum amount and it was found that the weight of kieselguhr should be equivalent to the metal used. The reduction temperature was 450°C. In the initial stages it was possible to get 65% of the total CO to liquid hydrocarbons and the rest to gaseous hydrocarbons. After five weeks of operation the yield had only dropped 17%. Since manganese was found to have the same favorable action as thoria and is less expensive, it was used to replace thoria, just as nickel was used to replace cobalt for the same reason.

In 1932, the same workers (34) used a nickel, manganese, alumina, kieselguhr catalyst in a pilot plant. The catalyst was prepared by precipitation from the nitrates with potassium carbonate followed by washing, drying and reduction. Revivification of the catalyst was done every 1,000 hours by extraction of the solid paraffin, using gasoline. The synthesis product contained 15-38% unsaturated hydrocarbons and had an octane number of 58. The ratio of gasoline, to oils above 220°C., to paraffin wax, was 4:1:0.2.

In 1932 Fischer, Roelen and Feist (35) recorded the superiority of a nickel catalyst over the cobalt catalysts that they had been using. This catalyst consisted of the oxides of nickel, manganese and aluminium precipitated on kieselguhr. The preparation is as follows: to a solution of 250 parts nickel nitrate.$6H_2O$, 50 parts manganese nitrate. $6H_2O$, 34 parts aluminium nitrate. $9H_2O$, in 600 pints of distilled water is added 60 parts of kieselguhr, the mixture

being at room temperature. Next is added a solution of 210 parts anhydrous potassium carbonate in 600 parts distilled water. The resulting mixture is then boiled and filtered. The precipitate is washed with 600 parts of hot water and is dried in an air stream at 110°C. The product can be used as a powder or as a coarse dried material. A yield of 130 cc. per cu. meter was reported in the initial stages of synthesis using this catalyst. After four weeks the figure had dropped to 120 cc. per cu. meter. These yields were for a $2H_2/1CO$ synthesis gas passed at four litres per hour over the above mentioned catalyst, where the metallic nickel content was four grams. The optimum synthesis temperature started at 190°C. with an increase to 210°C. towards the end of the run. As a regeneration step, a current of hydrogen was passed over the catalyst bed at a temperature of 450°C. This temperature was maintained for about four hours. It was found that gaseous ammonia with the hydrogen greatly extended catalyst life. After reduction the catalyst was again very active.

In another report by Fischer in 1943 (25) earlier statements would seem to be contradicted. This latter report states that nickel catalysts, with their tendency towards hydrogenation, are not suitable for synthesizing liquid hydrocarbons. In addition, at high pressure they form nickel carbonyls and are gradually carried out of the catalyst chamber.

Cobalt and nickel are relatively expensive metals. This fact has greatly stimulated the search for

cheaper catalysts. As a result a great deal of research has been conducted on iron catalysts,

Fischer and Tropsch in 1928 (37) reported on their experimentations using an iron-copper catalyst at atmospheric pressure. The product consisted of paraffins and olefins. The fraction oiling between 60° and 185°C. contained 70% mono-olefins. Decarriere and Antheaume (68) claimed an improvement when they used less copper in the iron-copper catalyst. Kodama and Fujimura (51) studied catalysts of iron-copper having the following ratios: 1:2, 1:1, 3:1 and 5:1. Little or no difference in catalytic activity could be observed in the four mixtures.

Japanese research workers (73) used iron, copper, kieselguhr and potassium carbonate in the ratio of 4:1:5:0.08. To some of this catalyst they added 0.8 parts of manganese. The yields were respectively 83 and 88 cu. cm. of liquid hydrocarbons per cu. meter of $2H_2/1CO$ synthesis gas. The oxygen from the CO in the synthesis gas appeared as carbon dioxide instead of as water as with cobalt and nickel catalysts. The optimum copper content was found to be 20-40% while the optimum potassium carbonate content was from 2-3%. If above 2.5% nickel was added to the catalyst, water formation took place. Important work on iron-copper catalysts was done by Eidus (17).

Iron catalysts can be made to produce about the same yield as cobalt does in the synthesis (25). It is desirable to have the gas richer in CO than H_2. The product, when analyzed, is more unsaturated and there are many more oxygen

compounds formed.

Information made available from Germany in June 1945 was emphatic in the statement that the use of iron catalysts in the synthesis was considered only as a wartime necessity, due to the shortage of cobalt, but iron catalysts were actually never used in commercial installations (78).

Summarizing the properties of iron catalysts (6) they are as follows: at one atmosphere pressure activity is lost in a few days, but at 7 atmospheres pressure good behavior can be obtained. When the activity is once lost it cannot be regained. The overall reaction may be represented as:

$$18CO + 10H_2 \longrightarrow C_9H_{20} + 9CO_2 \quad - 211{,}000 \text{ calories}$$

Table II

Duration of Life and Yields of Catalysts Recently Studied (23)

Catalyst	Recovery per cubic meter	Life till Decreased to 80% of Original Activity
Iron		
Fe-Cu-Mn-Silicagel 0.4% K_2CO_3	30-35 g.	8 days
Fe-Cu prec. on Kieselguhr	28 g.	8 days
Nickel		
Ni-Th prec. on Kieselguhr	100 g.	30 days
Ni-Mn-Al prec. on Kieselguhr	105 g.	45 days
Cobalt		
Co-Th prec. on Kieselguhr	110 g.	60 days
CO-Mn prec. on Kieselguhr	105 g.	Min.30 days
Co-Ni alloyed (Si)	85 g.	12 days
Co-Th-Cu prec. on Kieselguhr	105 g.	60 days

In 1938 the synthesis of high melting point wax on ruthenium catalysts at high pressures was reported (14) . Ruthenium was found to produce solid hydrocarbons more effectively than any other element of group VIII in the periodic table. At 100 atmospheres pressure and 195°C., 100 grams of paraffin wax and 50 grams of oil were obtained per cu. meter of gas. The catalyst proved to be very stable. Fischer and co-workers (27) tested a ruthenium powder catalyst. A low yield of hydrocarbons was obtained at atmospheric pressure. At approximately 90 atmospheres of pressure 120 grams of product per cu. meter was obtained.

Eighty to ninety percent of this amount was solid paraffin. Many syntheses have been carried out with this catalyst at pressures up to 1,000 atmospheres.

Recently two new syntheses have been announced, "naphthene synthesis" and "isosynthesis". No information is available on the former but some literature has been published on "isosynthesis" (14) . By this process isoparaffins are produced directly giving a gasoline fraction with a high octane number. The C_4 fraction is claimed to contain 90% isobutane. A robust massive iron catalyst is used at 200 p.s.i. and 300°C. Since reduction temperature is 850°C. little if any iron oxide is present. Catalysts reduced at lower temperatures than 650°C. contain some ferrous oxide. From the meager information available (6) the yield per pass is low, around one percent, so a high recycle must be used.

Information recently published (39), tells of

a new process developed since 1941 by Fischer, Pichler and Ziesecke, which produces large quantities of iso-paraffins. Ruthenium and cerium are thought to be the active metals used.

During the war German scientists at the Kaiser Wilhelm Institute conducted research in an attempt to perfect the "isosynthesis" (78). The best catalyst found proved to be one produced by the co-precipitation of alumina and thoria. Zinc oxide-alumina appeared to be nearly as active and was cheaper. If the carbon deposit was burnt off the catalyst every two weeks, it could be used continuously for over six months without appreciable decline in activity. Operating conditions were about 300 atmospheres pressure and 420-450°C. Lower pressures gave reduced yields while pressures above 300 atmospheres gave increasingly greater percentages of oxygenated products. At 1,000 atmospheres the principal product was dimethyl ether. Above 450°C. the product became principally naphthenic with excessive carbon deposition. Heat evolution was of the same order as for the normal synthesis. Twenty cubic centimeters of a two to four millimeter catalyst were found necessary for each ten litres of synthesis gas per hour. The yields from a zinc oxide-alumina catalyst using a $1H_2/1CO$ ratio gas were as follows:

Total yield of C_3+ = 120-130 grams per cu. meter
" " " C_3 = 20 grams per cu. meter.
" " " C_4 (90% isobutane) = 50-80 grams per cu. meter
" " " C_5+(97% iso-compounds) = 30-60 grams per cu. meter.

Synthesis of aromatics using chromium, molybdenum and thoria as catalysts was also studied. The conditions were 30 atmospheres pressure and 500°C. temperature. The poor yields obtained (8-10 grams per cu. meter, about 50% aromatic) le~~a~~d the workers to abandon this work.

All catalysts mentioned so far have been made by precipitation methods. The precipitate is usually obtained by the action of an alkaline carbonate on the metal nitrate followed by filtration and drying.

Besides precipitation, catalysts can be made by fusion of the metals followed by chemical treatment. Raney (62) evolved this method. Alloys of nickel or cobalt or the elements themselves are mixed with silicon or aluminium and fused in a furnace. The silicon or aluminium is then removed by means of sodium hydroxide to leave a skeleton catalyst. Thus a porous sponge catalyst is produced with a greatly developed surface and a high activity. It was found that sodium hydroxide was the best reagent with which to dissolve the silicon or aluminium. Potassium hydroxide could be used but other bases were unsuitable. Fischer and his associates (30) have reported that silicon alloys yield catalysts of higher activity than those obtained from aluminium alloys. In general they noted that alloyed catalysts lose their activity faster than catalysts prepared by the precipitation method but they are better heat conductors. Later Rapoport and Polozhintava (63) tested nickel and cobalt catalysts prepared in the above manner. The maximum yield, which resulted between 170-175°C., did not exceed 100 cc.

per cu. meter of synthesis gas using a nickel catalyst. With a cobalt catalyst, however, a maximum yield of 175 cc. per cu. meter was obtained at 200°C.

It is essential that a catalyst be produced which has as long a life as possible. Operating conditions greatly influence the life of a catalyst. It has been reported that the longest life possible is in the region of six months (75). The activity of cobalt catalysts may be restored by treatment with hydrogen at a relatively low temperature. Low temperature activations at a temperature of 200-215°C. are employed periodically. High temperature activations are conducted at 380-400°C. to clean the catalyst surface of some of the foreign compounds. The latter treatment should only be necessary after the catalyst has been in use for some time.

Many of the synthesis catalysts are made up of three ingredients: the catalyst metal or metals, one or more catalyst promoters and an inert carrier.

Naphtali (58) has stated that copper is beneficial with an iron or cobalt catalyst since it lowers the temperature necessary for the reduction of carbon monoxide. It is ineffective with nickel catalysts. Thoria and manganese, when precipitated with cobalt or nickel, appear to distort the metal surface giving a beneficial effect. Alkalies in small quantities favor the formation of paraffins, when used with iron catalysts. Maxted (54) found thoria the most effective promoter of the catalytic action of cobalt for production of hydrocarbons by the Fischer-Tropsch process.

A mixture of five parts cobalt oxide to one of thoria proved the best. Makino and his associates (53) investigated the influence of several elements and compounds upon iron catalysts. Of aluminium compounds only alumina showed an activating effect. If a copper promoter is replaced by silver the catalyst is weakened and more waxes are formed. Calcium, barium, bismuth, cadmium, lead and tin weakened the catalytic activity of iron.

In addition to kieselguhr as an inert carrier or support for cobalt and nickel catalysts, various researchers have recommended asbestos, magnesium carbonate, barium sulfate, silicon carbide, chromium oxide, aluminium oxide and silicates. Kieselguhr, however, is the generally accepted carrier. Eidus and his fellow workers (16) proved that the yield and properties of the product were dependent to some extent upon the type of kieselguhr used. Since it is necessary that much of the heat given by the exothermic reaction be conducted away from the catalyst Fischer and Meyer (29) attempted to find a heat conducting catalyst. They used graphites of different degrees of purity as carriers because they are much better conductors of heat than kieselguhr. The yields with graphite, however, were equally as low as with no carrier at all. Supporters for iron catalysts have not proved advantageous.

Process Variables

The yields and properties of the products of the Fischer-Tropsch Synthesis vary with changes of pressure, temperature, contact time, ratio of carbon monoxide to

hydrogen in the synthesis gas and diluents.

The original synthesis was conducted under high pressures varying from 100 to 150 atmospheres but instead of high yields of hydrocarbons a mixture of alcohols, aldehydes and hydrocarbons was obtained. Greatly reduced pressures (7 atmospheres or less) were later discovered to be required for the elimination of most of these oxygenated compounds and the increased production of paraffin compounds. The catalysts then in use however, were not active enough to produce practical yields. In 1925-1926 Fischer and Tropsch (36) succeeded in preparing a catalyst which could be used at atmospheric pressure. The resulting product consisted mainly of paraffins ranging from ethane to solid paraffin wax. Almost no oxygenated compounds were present. In the "normal pressure synthesis" the yield dropped from 130 to 100 grams per cu. meter of synthesis gas in four weeks. This was considered too rapid a drop in catalyst activity so research was continued. However, very recent reports from Germany state that it is this synthesis which was in common use there.

Industrial interest in the synthesis was accelerated by the discovery in 1936 of the "middle pressure" process (13). At pressures between 5 and 15 atmospheres an optimum yield of hydrocarbons was obtained and catalyst activity was not as greatly impaired. A production of 150 grams per cu. meter of synthesis gas was obtained initially and decreased to about 100 grams per cu. meter after 26 weeks of operation. This fact was explained by Fischer and Pichler (33)

on the basis that certain poisons, such as oxygen compounds, are hydrogenated to harmless products under the conditions of the "middle pressure" process.

Graph number one illustrates the yields obtained over a period of weeks when different operating pressures were used. Five atmospheres pressure is shown to give the least decline in yield for the cobalt catalyst employed. Graph number two shows the effect of variation of pressure on the average yields obtained again using a cobalt catalyst.

Table III

Yields[x] of Hydrocarbons at Different Pressures in Gms. per Cubic Meter (75)

Gauge Pressure Atm.	Solid + lq. Hydrocarbons	Paraffin Wax	Oil (above 200°C.)	Gasoline Fraction (below 200°C.)	Gaseous hydrocarbons including C_3 and C_4
0	117	10	38	69	38
1.5	131	15	43	73	50
5	150	60	51	39	33
15	145	70	36	39	33
50	138	54	37	47	21
150	104	27	34	43	31

[x] average yields per cubic meter of ideal gas over 4 weeks operation with a single passage of the gas over the catalyst and without revivification of the catalyst.

The synthesis of hydrocarbons from CO and H_2 has been found to be a temperature sensitive reaction. Tsuneoka

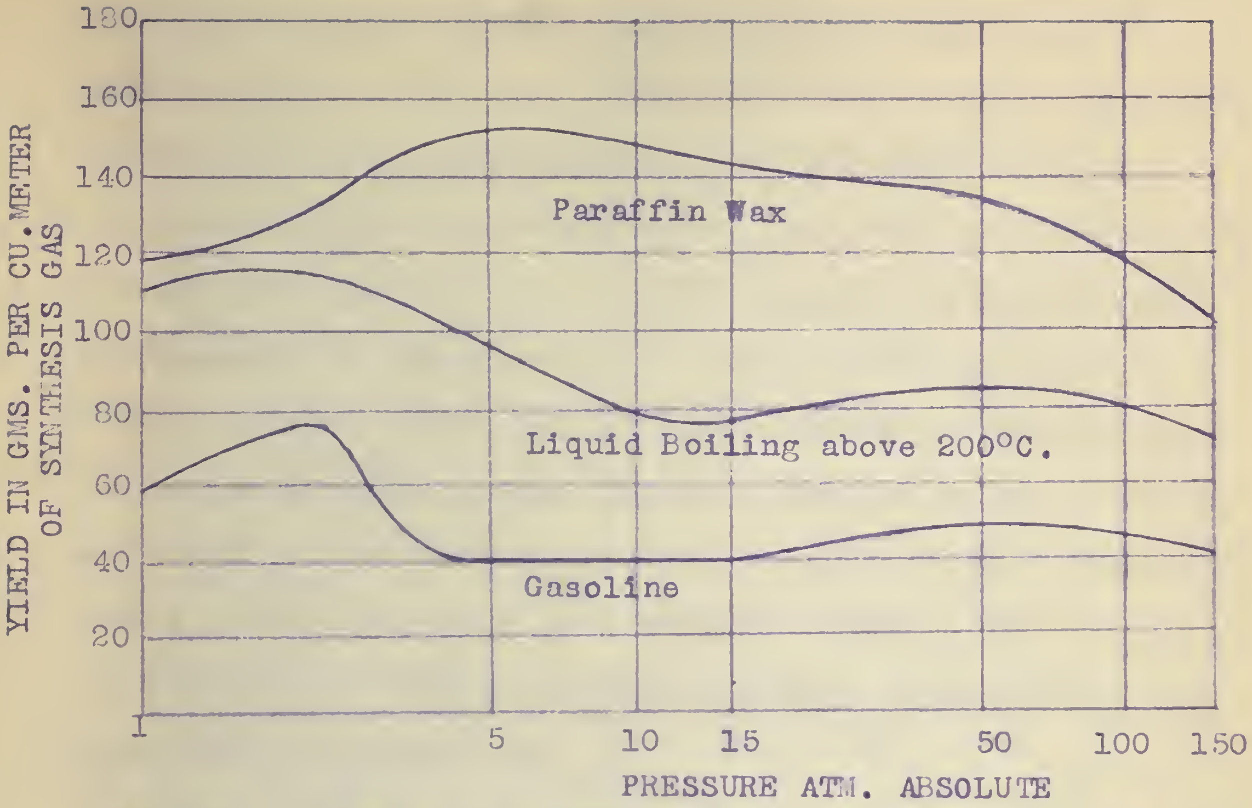


FIGURE 1 - EFFECT OF PRESSURE UPON YIELD OF HYDROCARBONS
($Co-ThO_2$-Kieselguhr Catalyst)

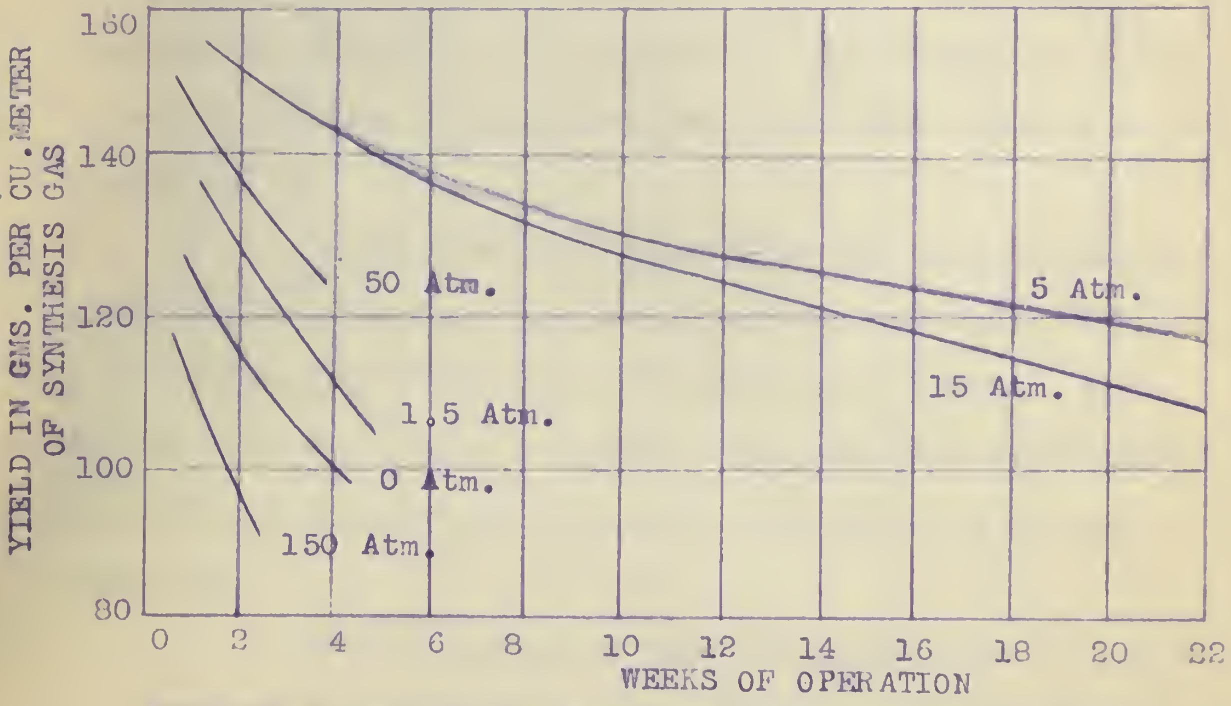


FIGURE 2 - EFFECT OF PRESSURE ON CATALYST ACTIVITY AND LIFE ($Co-ThO_2$- Kieselguhr Catalyst)

and Murata (72) working on cobalt catalysts have reported that even the most active catalysts give a slow rate of reaction below 175°C. and above 225°C. the reaction produces methane at the expense of the liquid hydrocarbon yield. The optimum synthesis temperature for cobalt catalysts lies between 195° and 200°C. A slight increase in temperature is necessary as the activity of the catalyst declines. Between 300 and 350°C. the methane reaction is predominant. The oxygen from the carbon monoxide appears in the reaction product as carbon dioxide and not as water at this temperature. Nickel catalysts behave in a similar manner. Iron catalysts are reported to produce maximum yields of liquid and solid hydrocarbons at 250°C. (6) .

The contact time is an important process variable. The allowable space velocities are very low - between 100 and 150 per hour based on catalyst volume. Any further increase in throughput is hampered by the difficult heat transfer problems arising from the exothermic nature of the reaction.

Myddleton (56) found that the time of contact greatly influences the properties of the product. A larger space velocity resulted in a product which contains more olefins but the yields drop off. The use of a multi-stage process with removal of the product between stages was suggested.

With constant throughput a change in the volume of catalyst in a convertor gives the same effect as changing the space velocity. Tsuneoka and his co-workers (70) have

experimented with variations of optimum length of catalyst tube with changes in tube diameter. Ten grams of cobalt-nickel catalyst were used with a flow of four litres per hour of synthesis gas. For 13 m.m. diameter tubing 50 cms. was the optimum length. If a tube was used which was shorter than the optimum, the average molecular weight of the liquid hydrocarbon product decreased and more gaseous hydrocarbons were produced. With a length which was longer than the optimum, channelling occurred giving reduced yields. With other variables constant, an increase in the charge of cobalt-nickel catalyst over a limiting amount to any convertor (keeping the same grams catalyst per c.c.) did not effect the yields of liquid hydrocarbons but it did increase the amounts of CO_2 and gaseous hydrocarbons. A charge under the optimum amount gave hydrocarbons which were more unsaturated and had a liquid product of lower molecular weight, and the yields were reduced.

Using a cobalt-thoria-kieselguhr catalyst (100:18:100) at 10 atmospheres pressure with two stage operation, Fischer and Pichler (33) studied the influence of contact time on yields and properties of the products. Eight grams of catalyst were used in the first stage and four grams in the second.

Table IV

Throughput /Hr./Gms.Cat. in litres	Temperature 1st Stage	Temperature 2nd Stage	Yield in grams per cu. meter: Condensed Hydro-carbons	Gasoline	$C_3^+C_4$	C_2	C_1	C_3^+
2.16	213.5	214	96	26	19	1	33	141
1.12	189	189	141	15	10	2	16	166
0.87	190	192	144	15	12	2	19	171
0.83	191	192	144	16	13	1.4	19	173
0.43	184	184	151	14	15	2	12	180
0.27	178	177	157	11	16	1	12	184
0.25	177	177.5	159	11	16	1	11	186

The condensed hydrocarbon is liquid at 10 atmospheres and room temperature.

These workers noticed the small amounts of C_2's formed during the reaction. This was explained by a discussion on mechanism of reaction which is dealt with in a later section. The yield of solid paraffin and higher hydrocarbons was found to decrease with increasing throughput. At maximum yield the product contained 48% solid paraffin, 44% liquid hydrocarbon and 8% C_3 and C_4. At a throughput of 2.0 litres per hour, 145 grams of C_3 hydrocarbons and higher were obtained of which 14% was solid paraffin, 73% liquid hydrocarbons and 13% C_3 and C_4. The greater methane formation was explained by the increased operating temperature. It was found that at constant temperature yields of C_3 hydrocarbons and higher dropped rapidly with increased throughput.

Much research has been conducted to determine

the best ratio of constituents to be used in the synthesis gas. The most generally accepted ratio for all but iron catalysts is a $2H_2/1CO$.

Fischer, Roelen and Feist (35) have recommended this mixture because it undergoes the required reaction at the highest rate and furnishes maximum yields of products per cubic meter of gas. When the synthesis gas contains more CO than called for in the stoichiometrical equation, the amount of liquid product and its unsaturation increases but the reaction rate becomes slower. More carbon dioxide is also produced. A hydrogen content in excess of the above ratio results in more gaseous products, more saturation and more rapid conversion. The influence of the gas ratio may be minimized by regulating the synthesis temperature so that it is higher for CO rich gas than for H_2 rich gas.

Herington and Woodward (49) have studied the effect of a high H_2/CO ratio in the inlet gas. The formation of hydrocarbons of lower molecular weight is favored. Using a ratio of 8.44 $H_2/1CO$ no oil or wax was obtained. The reaction favored was thus: $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$.

Myddleton (56) believes that a mixture known as blue water gas, $1H_2/1CO$, should be used with nickel and cobalt catalysts. The latter catalyst with this gas mixture gives an oil containing 50% olefins, while a gas of ratio of 2/1 with the same catalyst gave only 35% olefins. By means of two stage operation a gasoline of 65 octane number was obtained from the first stage and 68 octane number from the second stage. When blue water gas is used the olefins formed

in the reaction are not hydrogenated and since this reaction produces 7% of the total heat liberated, less heat is given out. This is advantageous.

The synthetic oil produced from a $2H_2/1CO$ gas was claimed to be so inferior in octane number that a cracking plant would have to be built. Here the loss in gasoline yield would be high - about 19% of the total throughput.

Underwood (56) strongly attacks the work done by Myddleton. By calculation it was shown that 25% more blue water gas was required than if the water gas was converted into synthesis gas of $2H_2/1CO$ ratio. A corresponding increase in the size of equipment would be necessary. The cracking of the product from $2H_2/1CO$ gas was thought to be more advantageous since the final octane number was 78 instead of from 65 to 68. Thus a considerable amount of tetra-ethyl lead was saved.

For iron catalysts a ratio of $1H_2/1CO$ is used but Fischer (25) recommends that the gas be richer in CO than H_2.

To produce pure synthesis gas would be expensive and needless. It is claimed that the process can operate satisfactorily with a diluent content as high as from 10 to 12%. Even higher amounts have been reported. Ostermeier (68) gives the following as being an average analysis of the gas used for commercial synthesis in Germany:

H_2	55.0%	CH_4	0.6%
CO	27.5%	N_2	2.7%
CO_2	14.0%	O_2	0.2%

Contrary to other investigations Fischer, Roelen and Feist (35) have reported that any dilution of the H_2-CO mixture results in a greatly reduced rate of reaction. Inert gases such as nitrogen and methane act as diluents as do the products of the reaction themselves. The advantage of working in stages, thus removing the product at the end of each stage, was pointed out.

Tsuneoka and Fujimura (71) have reported the effect of nitrogen, methane and carbon dioxide when using a nickel-manganese-thoria catalyst. It was found that gaseous mixtures with less than 20% of these diluents could be used without producing a disadvantageous effect on the reaction. With a 40% addition of nitrogen lower yields were obtained.

As can be seen experimental data is contradictory on the subject of diluents. Carbon dioxide is claimed to reduce the yield of hydrocarbons to the greatest degree. Fischer and Pichler have not obtained the same conclusions from their experimentation. Carbon dioxide seems to enter into the reaction, for in a mixture of CO_2, CO and H_2 the CO does not react until after the CO_2 has reacted.

Products

Fischer (24) has summed up the general properties of the products manufactured by the Fischer-Tropsch hydrocarbon synthesis. All are of high purity, pleasant odor and are colorless. Since they are entirely free from sulfur the

only treatment required is an alkali wash to rid them of traces of fatty acids.

As stated previously the properties of the products obtained from cobalt and nickel catalysts differ from those produced using an iron catalyst. Comparatively little work has been done on iron catalysts so data is not plentiful. It is known (6) however, that the latter produces straight chain paraffin waxes and a liquid which is 60-70% olefins and 30-40% paraffins. This higher olefin content gives the gasoline fraction an increased octane number.

Since cobalt catalysts are in general use in the Fischer-Tropsch synthesis of hydrocarbons, much more information is available in connection with them. The liquid products are mainly straight chain paraffins resulting in a low octane numbered fuel. Only minor amounts of aromatics, naphthenes and oxygenated organic compounds are present. The diesel fraction is of high quality (6). The following data has been reported (60) as general for a cobalt base catalyst:

Table V

	Wt. percent	Olefin content
Gases (Gasol)	8	50-55%
Kogasin 1 (200°C.P.)	60	30-35%
Kogasin II (Diesel Oil)	22	5-6%
Solid Paraffin	10	nil

End pt. of product	Octane No.	T.E.L. per U.S.gal. to give 70 octane
125°C.	62	0.9
150°C.	57	1.59
180°C.	47	3.63

Diesel oil has a cetane number of 100.

A more detailed analysis by fractions follows:

Gasol: Fischer and Koch (28) have described this as a mixture of the hydrocarbon series from ethane to butane with some pentanes. The percentage of unsaturates varies with experimental conditions. It has a calorific value of up to 23,000 cal. per cu. meter but because of its great value in synthesis work is not used as a fuel.

Kogasin I: Consisting of almost all open chain hydrocarbons, this fuel is entirely free of sulfur and resins (28). Because of the low octane number isomerization of the fraction is being considered (24). Solidification temperature is -60°C. Naphtali (58) has claimed that a 47 octane fuel can be brought up to 71.5 octane by the addition of 1 cc. tetraethyl lead per litre.

Kogasin II: This fraction proved to be superior to many gas oils in engine tests (28) and thus is considered by Fischer (24) to be a future source of transportation fuel. Kogasin II boils above 200-220°C. and has a solidification temperature of -30°C. Naphtali (58) has stated that because of the high hydrogen content of the oil, less is consumed per B.T.U. than in the case of ordinary oils.

Solid Paraffins: This fraction obtained by Fischer and Koch (28) had a melting point of between 75-85°C. Forty-six

percent of this did not dissolve in ether. This insoluble material melted at 92°C. Because of its high purity and good properties this was claimed to be very useful so would find a ready market.

The fraction boiling between 45-372°C. was investigated by Egloff, Nelson and Morrell (5). They have stated that 64% of 66 octane gasoline has been obtained in tests, by fractionation, cracking of naphtha and bottoms and polymerization of olefins in the gases. A total of 84.3% of product boiling in the gasoline range could be obtained. The yield of product expressed in percentage by volume was as follows:

Light gasoline	29.1%
Reformed naphtha	26.8%
Cracked gasoline from bottoms	22.6%
Polymerized gasoline	5.8%
	84.3%

Considering synthetic fuels in general, leading authorities have compared the products of the Fischer-Tropsch synthesis of hydrocarbons with those of the Bergius hydrogenation process. They find that the two are complementary rather than competitive. The latter yields high octane gasoline but only mediocre diesel oil. The Fischer-Tropsch process on the other hand yields poor gasoline but excellent diesel fuel. Synthetic lubricating oils can be made from Fischer-Tropsch Kogasin but this is impossible from the products of the Bergius process.

Yields

The theoretical yield from the Fischer-Tropsch synthesis of hydrocarbons using one cubic meter of gas containing two parts of H_2 to one part of CO is 208 grams. Underwood (75) has reported that yields of 130 to 140 grams have been reached commercially in a one stage operation, while recent figures from Germany report yields of 160 gms./cubic meter of feed gas. By recycling it is possible to transform almost 100% of the gases into liquids but the economical aspect of this process makes it impractical. Fischer and Pichler (32) have developed a stepwise process which has been applied on a laboratory and pilot scale to produce 140-150 grams per cu. meter of synthesis gas. Using the accepted $2H_2/1CO$ synthesis gas, a cobalt-thoria catalyst and a space velocity of 201cc. per hour per gram of unreduced catalyst, Haxted (54) has reported a yield of 128.8 grams of hydrocarbon per hour per cu. meter of gas, or 0.026 grams per hour per gram of catalyst. The gas contraction was 64.3%.

Possible commercial yields have been stated in more meaningful terms; — 1.4 gallons of gasoline per 1,000 cu.ft. of synthesis gas or 3-5 gallons of gasoline per 1,000 cu. ft. of methane.

Valuable by-products may be obtained from the synthesis. Storch (68) has written that investigators have found that fatty acids constitute about 0.35% by weight of the liquid hydrocarbon yield. Formic, acetic, propionic and butyric acids have all been separated and identified:

acetic acid makes up about two-thirds of the total fatty acids which are soluble in water. Fatty acids from C_5 to over C_{10} were found in the hydrocarbon product. Komarewsky and Riesz (52) have stated that since 1936 catalytic oxidation of synthetic wax from the Fischer-Tropsch synthesis has been used to make fatty acids. The product consists almost entirely of saturated molecules containing both even and odd numbered carbon atoms. Air is used for the oxidation. The resulting exothermic reaction yields monocarboxylic acids and small amounts of alcohols. From a 6,000 barrel per day plant now being designed, 200,000 pounds per day of crude alcohol are expected (64).

In a report published in May 1945 (66) the "OXO process" which has been in operation in Germany, is discussed to some extent. By means of this process Fischer-Tropsch C_{12}-C_{17} olefins are treated at 150°C. and 150 atmospheres pressure over a cobalt catalyst to produce aldehydes. These are then reduced to alcohols over a nickel catalyst at 180°C. and 150 atmospheres pressure. The alcohols are then converted into sulphonic ester soaps.

No lubricating oil fraction is present in the synthesis product. To remedy this situation methods were devised in Germany to manufacture lubricating oil from the Kogasin. Among the methods reported are the polymerization of fractions rich in olefins with aluminium chloride; the chlorination of a Kogasin fraction and polymerization without the addition of aromatics; and the alkylation of aromatic hydrocarbons with chlorinated fractions according to the

Friedel-Crafts reaction. The above methods are reported to produce a lubricating oil which has excellent viscosity properties.

In summation, the literature recognizes the fact that the Fischer-Tropsch synthesis is still in its infancy. Many problems still await solution. Komarewsky and Riesz (52) believe that future research should have as its objective the search for a more active catalyst which will react at a higher space velocity; the development of catalysts to produce a specific product such as naphthenes, isoparaffins or waxes; a sulfur-resistant catalyst and the development of a catalyst which will make use of, in a more satisfactory manner, a gas made up of $1H_2$ and 1CO. Boomer (6) has stated that the heat transfer problem is in need of solution. Particularly from the viewpoint of industry a fluid catalyst flow unit in place of the fixed bed type now used would reduce the steel requirements. Intensive research is necessary to substantiate the possible use of oil in the catalyst chamber to take away the heat of reaction. The relationship between the period of catalytic life and metal loss as carbonyls must also be investigated.

THE MECHANISM OF REACTION ON FISCHER-TROPSCH CATALYSTS

It is evident from the preceding discussion that Fischer-Tropsch catalysts are of two types, iron and cobalt. The nickel catalysts are similar to cobalt and most of the reactions they undergo are similar. The iron type of catalyst yields large amounts of olefins and carbon dioxide is the main oxygenated product. Cobalt catalysts, on the other hand, yield essentially paraffin hydrocarbons and water is the main oxygenated product. All Fischer-Tropsch catalysts are characterized by high sensitivity to temperature and to poisons such as sulphur. These fundamental characteristics of the catalyst in conjunction with data obtained by operating the catalyst at varied temperatures, pressures and synthesis gases, provide a basis for postulating a reaction mechanism.

The literature on reaction mechanism of Fischer-Tropsch catalysts reveals that by far the greater amount of experimental work has been carried out on cobalt catalysts. With the iron catalyst, reactions are rather uncertain and all observations point to an inherently more complex reaction mechanism than that for cobalt.

Over cobalt catalysts the overall reaction is empirically (7):

$$nCO + (2n + 1)\ H_2 = C_nH_{2n+2} + nH_2O$$

$$H = -267{,}600 \text{ calories approximately}$$

Assuming that the average carbon number of the hydrocarbons produced is nine, "n" has a value of nine in the above reaction.

Likewise, over iron catalysts the overall reaction is empirically (7):

$$2nCO + (n + 1)\ H_2 = C_nH_{2n+2} + nCO_2$$

$$H = -211,000 \text{ calories approximately}$$

Here "n" has a value of nine, if the average carbon number of the hydrocarbons produced is assumed to be nine.

The suitability of any proposed reaction mechanism can be tested in two general ways. Firstly, by means of the proposed mechanism it must be possible to explain observed physical phenomena resulting from use of the particular catalyst. Secondly, the mechanism if at all accurate should be a practical aid in predicting or interpreting certain behaviors of the catalyst when subjected to treatment other than that which is normal for it.

Cobalt catalysts are generally associated with the production of characteristic products and reactions, and it is by consideration of these factors that the several existing reaction mechanisms have been formulated.

The following characteristics have been observed in connection with the Fischer-Tropsch synthesis, and their role in the formulation of a reaction mechanism will be discussed.

1. The initial reaction of the synthesis gas ($CO + 2H_2$) over a freshly reduced cobalt catalyst at about 200°C. and atmospheric pressure produces methane and CO_2 for several hours, after which time liquid hydrocarbons and water are produced (9).

2. Synthesis of liquid hydrocarbons occurs mainly between the temperature range of 175°C. and 225°C. Above 225°C. much methane is formed (9).

3. Methane formation continues up to a temperature of 325°C. and throughout this temperature range carbon dioxide is the principal oxygenated product which is produced. (9).

4. Activity of the catalyst drops off after about a week of normal use but can be restored by a low temperature hydrogen activation at about fifteen degrees above normal operating temperature and at atmospheric pressure. A large contraction results from this activation and for a short while methane and carbon dioxide are given off, after which liquid hydrocarbon synthesis again takes place (49).

5. Increasing the pressure to about fifty atmospheres results in the formation of oxygenated compounds (36). Some experimenters claim that some oxygenated compounds are produced even at atmospheric pressure (19).

6. Carbides have always been detected on a cobalt catalyst during synthesis of Fischer-Tropsch oils.

7. During the production of liquid hydrocarbons the ortho-para hydrogen conversion is inhibited (9, 10).

8. The introduction of a small amount of ethylene into the synthesis gas results in the production of organic oxygenated compounds at normal pressure (67).

9. During synthesis of liquid hydrocarbons over the catalyst the water-gas shift is inhibited (9, 10).

This shift is represented by the following reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

During the synthesis the equilibrium of the above reaction goes to the left.

10. A high hydrogen to carbon monoxide ratio in the synthesis gas favors the formation of lower molecular weight hydrocarbons (optimum ratio of H_2:CO is 2:1) (49).

11. Poisoning of the synthesis gas by addition of as much as 33.5 milligrams of sulphur per gram of catalyst results at first in an increased production of liquid hydrocarbons if the temperature is raised a compensating amount above operating temperature. However, when revivification of the catalyst by hydrogen is attempted, the catalyst is irréversibly poisoned (49).

12. The catalyst has a life of from six months to a year and after this period it cannot be revivified by a high temperature hydrogen activation (7).

13. After a high temperature reduction of the oxide catalyst with hydrogen, synthesis of long chain liquid hydrocarbons will not result unless a proper conditioning procedure is employed.

Among the several reaction mechanisms which have been advanced since the discovery of the synthesis process, those involving the formation of intermediate metallic carbides (38) serve to explain the majority of the characteristic reactions observed over a cobalt catalyst. Furthermore, there is good reason to believe that Fischer-Tropsch catalysts are entirely carbidic during synthesis(50).

Consequently a brief discussion on the properties of metallic carbides (50) will serve to simplify any subsequent reaction involving the intermediate formation of carbides. Emphasis will be placed on the properties of cobalt carbides but those on nickel and iron are similar.

If carbon monoxide is passed over the surface of a reduced cobalt mass, a carbide of the metal corresponding to the empirical formula Co_2C, will be produced (2,3,4). Metallic carbides are produced quantitatively at temperatures below 225°C., whereas a mechanical mixture of the quantitative amount of carbide with a surplus of elemental carbon is produced above this temperature. It would seem, therefore, that 225°C. is the critical temperature for complete carbiding of cobalt.

On hydrogenation at 275°C., or treatment with hydrochloric acid, the low temperature carbide is almost quantitatively decomposed to methane and small amounts of higher hydrocarbons. The high temperature carbide when treated with hydrogen, yields methane in equal amount to the low temperature carbide. Acid treatment, however, reveals that in addition to the carbidic carbon there is present a quantity of elemental carbon.

The upper temperature limit of the Fischer-Tropsch synthesis corresponds to the temperature at which elemental carbon will start to form on the catalyst surface. It has not been definitely shown that carbon formation seriously affects the synthesis. However, if carbon

formation results in the obliteration of active surface centres by the production of irreducible residues on the surface, poisoning of the catalyst would be effected. It will be shown presently that the amount of carbon formation varies directly with the time of carbon monoxide treatment. If as suggested, carbon formation could act as a deactivating agent, then perhaps the limited life of the Fischer-Tropsch catalysts could be attributed, at least partly, to this cause. Reduction of catalyst life through loss of active surface metal by carbonyl formation possibly also occurs (26).

Temperatures, time, and method of treatment of the reduced cobalt with carbon monoxide have a direct bearing on the amount of metal carbide formed (4). Low temperature carbon monoxide treatment at about 225°C. followed by a relatively short high temperature treatment at 300°C. results in the production of greater amounts of carbide than a single treatment at the high temperature for a relatively short time. (Compare with characteristics of cobalt catalyst, number 13.) At equal temperatures the percentage of carbide formed varies inversely with the time of carbon monoxide treatment and the amount of elemental carbon formed. The following mechanism of carbide formation is offered on the basis of these foregoing phenomena (50):

$$(1)\ 2CO + \underset{\text{(surface)}}{Co} \longrightarrow \underset{\text{(surface)}}{Co - C} + CO_2$$

The carbon present as surface carbide can probably diffuse (but not too rapidly) into the interior of the metal lattice.

$$(2)\ \mathrm{Co - C + Co} \dashrightarrow \underset{\text{(lattice carbide)}}{\mathrm{Co_2C}}$$

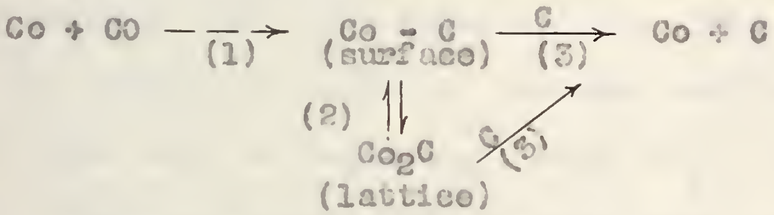
Both the lattice and the surface carbide are capable of decomposing to form elemental carbon and metal.

$$(3)\ \underset{\text{(lattice)}}{\mathrm{Co_2C}} \dashrightarrow \underset{\text{(elemental)}}{\mathrm{C}} + 2\mathrm{Co}$$

$$\underset{\text{(surface)}}{\mathrm{Co - C}} \dashrightarrow \underset{\text{(elemental)}}{\mathrm{C}} + \mathrm{Co}$$

The assumption must also be made that elemental carbon catalyzes reaction 3.

(4) The combined reactions may be shown thus:



The mechanism explains the large amount of carbide obtained by the two stage carbon monoxide treatment. At 225°C. reactions 1 and 2 proceed. When the temperature is raised the velocity of these reactions increases and Co_2C is produced quantitatively. Reaction 3 however, is not induced to any considerable extent at this time since there is no elemental carbon formed to catalyze it. Raising of temperatures or continuation of carbon monoxide treatment would form sufficient elemental carbon to catalyze reaction 3.

Craxford and Rideal by studying rates of reaction on Fischer-Tropsch catalysts have shown that reaction 1 in the mechanism just cited is not sufficiently rapid to account for the CO_2 formation (9). In place of this they have set forth the following mechanism:

$$(1)\ Co + CO \dashrightarrow Co - CO \text{ (chemisorption)}$$

$$(2)\ Co - CO + CO \longrightarrow \underset{\text{(surface carbide)}}{CoC + CO_2}$$

These are both surface reactions and correspond to the observed rate of initial carbide formation. As in the previous mechanism, these initial surface reactions are followed by diffusion of surface carbide into the lattice with subsequent formation of bulk carbide.

Fischer-Tropsch catalysts belong to the interstitial or nonionic lattice type of carbide (as distinguished from the ionic or salt like lattice)(45). This type of lattice may consist of stable or unstable carbides. Only the unstable types such as Fe_3C, Co_2C, Ni_3C, Fe_2C, Mn_3C are commonly formed on Fischer-Tropsch catalysts. All of these carbides are similar in their behaviour towards hydrogen, namely, they can be readily reduced to form methane. Furthermore, these carbides if present in an activated Fischer-Tropsch catalyst must have a carbon-atom radius to metal-atom radius equal to or greater than 0.58 (50).

Fischer and Tropsch (36) were the first to advance the "carbide theory" of the formation of hydrocarbons for the cobalt-copper catalyst. They postulated (37) the primary formation of unstable finely divided carbides which could be reduced at comparatively low temperatures by hydrogen to form methylene or complex molecules containing three to four carbon atoms.

$$CO + 2Me = MeC + MeO$$

$$MeC + MeO + 2H_2 = 2Me + CH_2 + H_2O$$

It is probably more correct to assume that the original carbide

is reduced to a lower carbide and not to the metal. The products of these initial reactions could subsequently undergo polymerization to higher molecular weight hydrocarbons. Polymerization of the complex molecules would eliminate the possibility of forming ethane or ethylene, but nevertheless these are found in the final product. Thus perhaps, the initial reaction with hydrogen involves the formation of both methylene and complex carbon molecules. Another alternative suggested by Fischer and Tropsch is the spontaneous formation of large hydrocarbon molecules on the surface which subsequently undergo cracking to lower hydrocarbons. This they believe is most likely, since thermodynamic considerations are indicative of such a reaction. In all the possibilities suggested, hydrogenation of olefins follows as a final step.

As an alternative to the "carbide theory" other workers in this field of research attempted to formulate a reaction mechanism wherein the formation of intermediate compounds was a primary step in oil synthesis. Two of the earliest workers were Elwin and Nash (19), and they attempted to correlate the production of small amounts of oxygenated compounds at atmospheric pressure with the reaction mechanism on the catalyst surface (characteristic #5). The catalyst used by these early experimenters consisted of a reduced mixture of manganese, cobalt and copper oxides. At atmospheric pressure the following reactions are possible which would result in the formation of oxygenated compounds:

$$2CO + 4H_2 = C_2H_5OH + H_2O$$

$$3CO + 5H_2 = CH_3COCH_3 + 2H_2O$$

$$2CO + 2H_2 = CH_3COOH$$

It was suggested that the non oxygenated liquid hydrocarbons resulted from the intermediate formation of alcohols; the alcohols then undergoing dehydration, polymerization and hydrogenation to give a Fischer oil.

Methane formation is accounted for by the following reactions (characteristic #5):

$$CO + 3H_2 = CH_2O + 2H_2O = CH_3OH + H_2 = CH_4 + H_2O$$

$$CO + H_2O = CO_2 + H_2$$

This mechanism for methane formation has a drawback, since formation of formaldehyde and methyl alcohol has not definitely been established at atmospheric pressures. No attempt to relate the foregoing reactions to possible surface catalysis was made.

Elvin (18) further advanced the idea of intermediate oxygenated products by suggesting that possibly the intermediate formation of carbonyls was a primary step in the formation of hydrocarbons. He worked with a cobalt-manganese-copper catalyst, and observed some volatalization of copper which could result from carbonyl formation. He points out that although copper is not a catalyzing agent for the reaction

$$CO + 3H_2 = CH_4 + H_2O$$

metal carbonyls (e.g. CuC.O) might function in some way to promote the above reaction.

The most comprehensive theory admitting of the

formation of oils through intermediate oxygenated compounds was advanced by Smith, Hawk and Golden (67). They too used a reduced cobalt-copper-manganese oxide catalyst to confirm their theory. Since passage of hydrogen over an activated catalyst produced mostly methane and other lower hydrocarbons, the possibility of higher hydrocarbon formation via the carbide became questionable. Secondly, the formation of very high hydrocarbons in one step followed by cracking seemed unlikely. Passage of longer chain hydrocarbons over the catalyst left these oils comparatively unchanged, whereby it was concluded that cracking of higher hydrocarbons did not occur. A similar treatment with ethylene put in doubt Fischer's suggestion of extensive polymerization, since higher hydrocarbons did not result. However, water gas containing at least ten percent ethylene, when passed over the catalyst, did yield considerable quantities of oil containing significant amounts of oxygenated compounds. These oils and oxygenated compounds when put in contact with the catalyst underwent some reaction whereby the oxygenated compounds were absent from the resulting product. These facts were the major premises upon which Smith, Hawk and Golden based their reaction mechanism.

Firstly, it seemed that on the catalyst surface, water gas formed complex molecules which might have decomposed to give an olefin (e.g. ethylene) and water. Alternatively, the complex may have combined with ethylene or another olefin to produce oxygenated compounds, which may have passed into the product, or undergone dehydration to

unsaturated residues. These residues might in turn polymerize to form higher hydrocarbons. Some saturation of these hydrocarbons could be brought about by the presence of hydrogen on the catalyst surface. The presence of carbon monoxide would tend to counteract the reaction by which unsaturated residues are polymerized and result in a more unsaturated product. Lastly, the presence of some carbon dioxide is probably due to the rapid elimination of this gas from the other intermediate products with which it forms.

Recently Crawford and Rideal (9, 10) have performed experiments which have lent considerable support to the "carbide theory". The mechanism of the formation and reduction of carbides has been enlightened by measurement of the rates of these reactions over the catalyst. A cobalt-thoriumoxide-kieselguhr catalyst with the compoents in the ratio of 100:18:100 was used.

The rates of the following reactions were measured:

1. $2Co + 2CO = Co_2C + CO_2$
2. $Co_2C + 2H_2 = 2Co + CH_4$

During the synthesis the catalyst was in contact with hydrogen and carbon monoxide and production of hydrocarbons might have resulted from the reaction:

$$Co_2C + H_2 \longrightarrow CH_2 + 2Co$$
↳ higher hydrocarbons

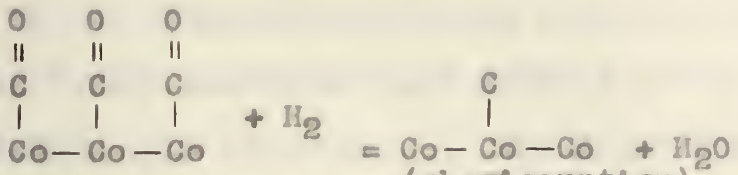
$$3.\ CO + 2H_2 \longrightarrow CH_2 + H_2O$$
↳ formation of hydrocarbons

The formation of Co_2C by reaction 1 was relatively rapid in comparison to the formation of carbide on an ordinary

precipitated and reduced cobalt sample, thus indicating that Fischer-Tropsch catalysts are more reactive towards carbide formation. Reaction 2 occurred at a greater rate than reaction 1. The overall reaction as represented by reaction 3 was faster than 1 or 2.

In view of these results, carbides could never accumulate on the catalyst because they are reduced by reaction 2 faster than they are formed by reaction 1. This is not true however, since it has already been mentioned that during the Fischer-Tropsch synthesis the catalyst is almost wholly carbidic. Gothel (44) gave further support to this fact by measuring the electrical conductivity of the powdered catalyst during synthesis and showing that it varied in such a way as to denote increasing carbiding as the synthesis proceeded. Consequently, carbide must be formed initially by a reaction more rapid than reaction 1 and 2.

The alternative to reaction 1 is that carbon monoxide is first adsorbed on the surface and,in the presence of hydrogen, a surface carbide is formed.



$$\begin{array}{ccccc} O & & O & & O\\ \| & & \| & & \|\\ C & & C & & C\\ | & & | & & |\\ Co & - & Co & - & Co \end{array} + H_2 = \begin{array}{ccccc} & & C & & \\ & & | & & \\ Co & - & Co & - & Co \end{array} + H_2O$$

(chemisorption)

$$Co - CO + H_2 = Co - C + H_2O$$

(surface carbide)

This reaction is much faster than reaction 2. In a discussion of carbides the identical reaction was mentioned where free carbon monoxide reacted with the adsorbed carbon monoxide to give carbon dioxide and the carbide

i.e. $Co - CO + CO = Co - C + CO_2$
(surface carbide)

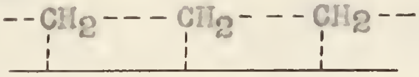
This accounts for the initial production of carbon dioxide from a cobalt catalyst. Once a surface carbide is built up, the reaction with hydrogen takes place and water is formed. The formation of water as the main oxygenated product during synthesis lends support to the occurrence of the above reaction.

It might seem anomalous that water should be formed, since a cobalt catalyst at 200°C should promote the water-gas shift reaction, and therefore carbon dioxide should remain as the main oxygenated product throughout the synthesis. On a Fischer-Tropsch catalyst, however, the reaction is inhibited up to a temperature of 250°C. - 300°C., whereupon the production of carbon dioxide displaces the production of water.

Smith, Hawk and Golden (67) pointed out that one of the chief weaknesses of the "carbide theory" lies in the fact that upon reduction with hydrogen, the product is almost entirely methane, and only by reduction of the carbide with dilute acid are higher hydrocarbons obtained. Experiments on the ortho-para hydrogen conversion on the catalyst surface during synthesis were carried out in an attempt to account for this behavior. It was found that when the synthesis produced hydrocarbon oils, the ortho-para conversion occurred to a very limited extent, and when methane was produced or there was no reaction the conversion occurred freely. This is equivalent to saying that when oils are obtained there is very little atomic chemisorbed hydrogen present on the catalyst surface and the reaction must be

proceeding by way of molecular hydrogen. The reverse of this is true when methane is formed. Furthermore, it has been shown that the ortho-para hydrogen conversion is not catalyzed by metallic carbide but occurs readily on a bare metal surface. Thus, the inhibition of the conversion during oil synthesis is probably due to a large surface concentration of carbide. Part of the inhibition may also be due to the presence of small amounts of ethylene. Hence the formation of large amounts of oil goes hand in hand with a large surface concentration of carbide and a small amount of chemisorbed hydrogen.

On the basis of the preceding experimental evidence the following reaction mechanism for the formation of long chain hydrocarbons on the catalyst surface has been offered. Firstly, the reduction of the separated carbon atoms in the cobalt carbide by molecular hydrogen leads to the formation of separated methylene groups chemisorbed on the catalyst surface. If conditions are such that carbide is being built up faster than it is reduced then there will be present only a small amount of chemisorbed hydrogen and under these conditions the methylene groups will combine to form longer chains. The chemisorption probably occurs in such a way that a giant molecule is formed on the surface, from which fragments may be broken off.



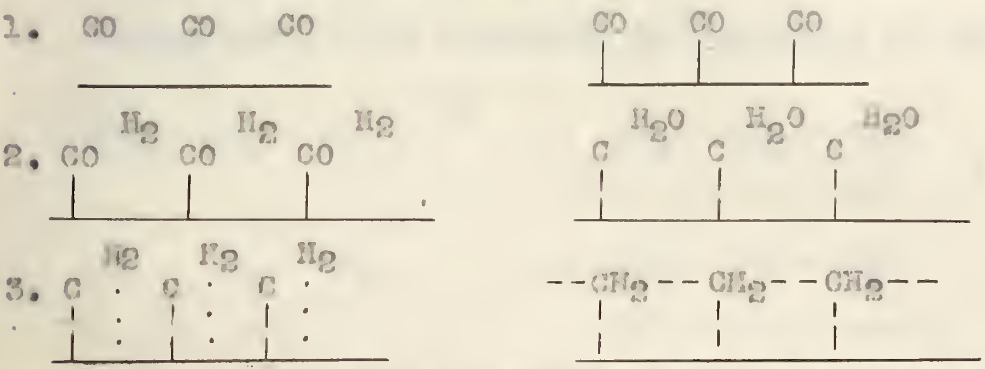
$$--CH_2---CH_2---CH_2--$$

Further experiments showed that cracking of hydrocarbons on the catalyst surface occurred only if chemisorbed hydrogen was present. It was therefore concluded that

the cracking of the large hydrocarbon molecules and desorption of hydrocarbon chains chemisorbed on the catalyst surface was caused by chemisorbed hydrogen. Thus the size of the hydrocarbon molecule formed during synthesis depends on the amount of chemisorbed hydrogen present, molecules of indefinitely large molecular weight forming when a minute amount of chemisorbed hydrogen is present, long chain hydrocarbons in the presence of slightly greater amounts and methane in the presence of large amounts. Indeed the initial formation of methane in the Fischer-Tropsch synthesis probably arises from the fact that carbide is just being built up and there is a large free metallic surface upon which a great deal of hydrogen is chemisorbed, immediately reducing the methylene groups to methane. The following (10) are a number of pictorial examples showing in a simplified manner how hydrocarbons are formed by means of the aforementioned mechanism:

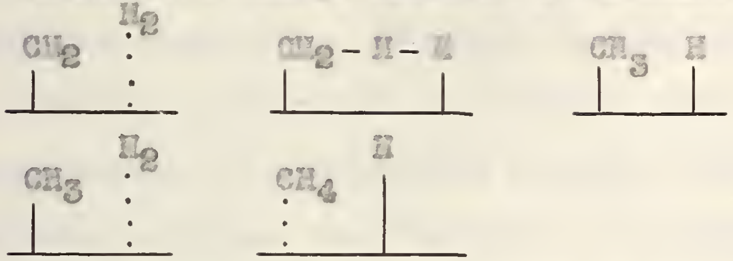
Legend

------ Van der Waal's adsorption
——— Chemisorption
— — Partial valencies of a transition state

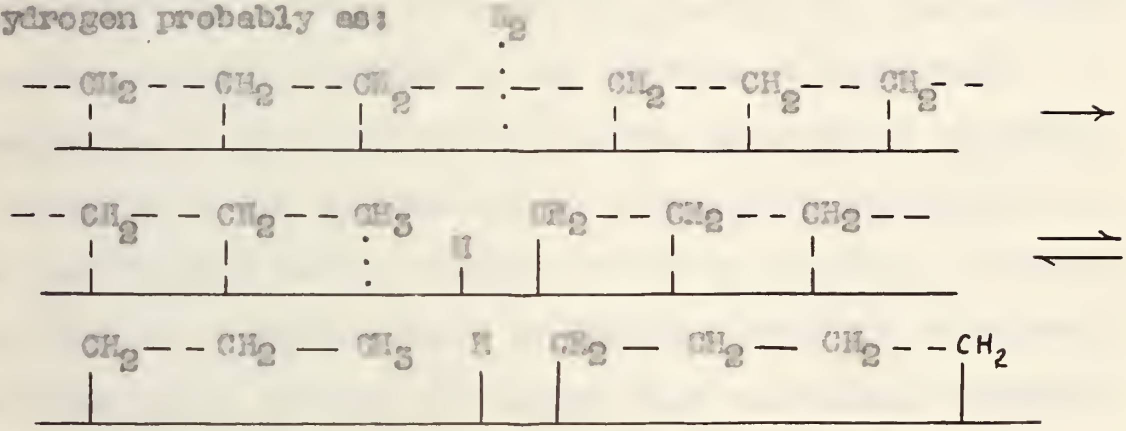


Macromolecules form in the presence of small amounts of chemisorbed hydrogen and subsequently undergo cracking and hydrogenation.

3 (a). Hydrogenation of a methylene group to methane in the presence of large amounts of chemisorbed H_2

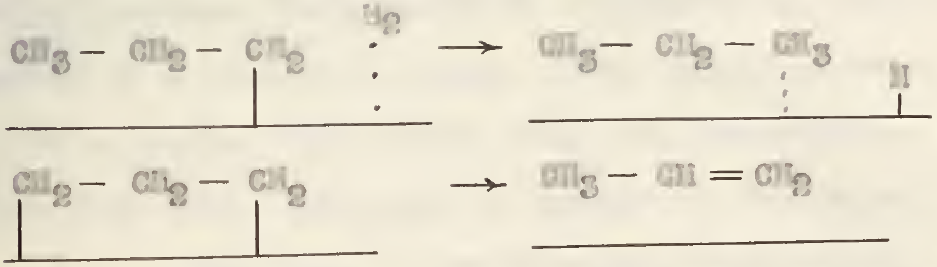


4. The macro molecules are disrupted by interaction with hydrogen probably as:



An equilibrium is set up in this process, namely polymerization of CH_2 groups ⇌ hydrogenation - cracking In the presence of small amounts of chemisorbed hydrogen equilibrium is shifted to the left and in the presence of large amounts of chemisorbed hydrogen the equilibrium is shifted to the right.

5. Desorption of the fragments of paraffins or olefins



The results observed by Smith, Hawk and Golden when ethylene was introduced into the synthesis gas passing

over a cobalt catalyst, namely that oil and organic oxygenated compounds were produced, can be explained on the basis of the foregoing mechanism. Ethylene is very strongly adsorbed on the catalyst surface and the overall result is to decrease the concentration of chemisorbed hydrogen allowing long chain hydrocarbons to form. The formation of oxygenated compounds is explained by the fact that the ethylene competes with the carbon monoxide for the surface with the net result that the amount of carbon monoxide adsorbed on the surface is decreased. Consequently, a good deal of the carbon monoxide is adsorbed not directly on the surface but in a secondary adsorption layer and is held rather weakly. It is not unlikely, therefore, that the molecule which is desorbed from the secondary layer will still contain the oxygen from the weakly adsorbed carbon monoxide.

Organic oxygenated compounds are also produced in the Fischer-Tropsch process by increasing the operating pressure (33). An increase in the pressure can have no great effect on the amount of chemisorption but it will affect the adsorption in layers above the surface. Thus in addition to the carbon monoxide adsorbed directly on the catalyst surface, there would be a quantity of carbon monoxide adsorbed in a secondary layer. This weakly adsorbed layer, as with ethylene, will bring about the formation of a hydrocarbon that still contains the oxygen of the carbon monoxide.

Operating at temperatures considerably above normal will result in methane formation (9, 10). This is probably due to the presence of less carbide on the catalyst

surface at the elevated temperature and hence more chemisorbed hydrogen would be available for desorbing methylene groups before they are polymerized.

Herington and Woodward (49) found that the introduction of small amounts of sulphur into the synthesis gas increased the yield of heavier hydrocarbons. Addition of more sulphur eventually caused a decrease in the total yield at normal operating temperature but the yield could be brought up by raising the temperature. In the latter case lighter hydrocarbons were formed. All the sulfur remained on the catalyst surface probably as cobaltic sulfide or cobaltous sulfide. A low temperature activation with hydrogen caused almost complete poisoning of the catalyst. In all cases excess amounts of sulfur resulted in complete loss of activity.

From these observations it was surmized that the catalyst surface consisted of active centres of two types, which for convenience, were called types A and B. Type A was probably cobalt carbide and was responsible for the formation of methylene groups which could polymerize. Type B was probably bare metal and was responsible for the chemisorption of hydrogen.

The increased yields of long chain hydrocarbons on the introduction of sulphur was likely due to the preferential poisoning of centres of type B while centres of type A were resistant to sulphur. Consequently only small amounts of chemisorbed hydrogen were present on the catalyst surface allowing the polymerization of methylene groups. On

low temperature activation with hydrogen the resistance of centres of type A to sulphur was reduced resulting in a redistribution of the sulphur and hence in a reduced activity of the catalyst. The fact that lower hydrocarbons are produced at higher temperatures with sulphur present is not unusual since at an increased temperature less of the catalyst can exist as carbide.

On the basis of the preceding mechanism a theoretical explanation for the particular method used in conditioning the catalyst, the effect of a high or low hydrogen to carbon monoxide ratio in the feed gas and the revivifying effect of the low temperature hydrogen treatment, was offered. It was found that if the catalyst temperature was not lowered sufficiently below operating temperature after the high temperature hydrogen reduction, large amounts of methane and very small amounts of oil were produced. Furthermore, excessive amounts of carbon dioxide and water were produced. The carbon dioxide in this case was probably produced by the water-gas shift reaction:

$$CO + H_2O = CO_2 + H_2$$

Since this reaction was probably promoted by bare metal surface it was suggested that under these conditions the catalyst surface consisted mostly of centres of type B. Thus a large part of the surface was available for chemisorbed hydrogen and methane production could be expected. Proper conditioning will insure plentiful centres of Type A throughout the synthesis. Also on the basis of the "active centre" conception it is likely that the activity of the most

active points on the catalyst is so high that the introduction of synthesis gas, without lowering the temperature sufficiently, would raise the local temperature of these spots far above the bulk temperature of the catalyst and as is usual with high temperature operation, methane would result.

Under otherwise similar conditions a high hydrogen to carbon monoxide ratio in the synthesis gas produces no higher hydrocarbons (49). The contractions obtained were such as to indicate the reaction:

$$CO + 3H_2 = CH_4 + H_2O$$

This again is attributed to the catalyzing effect of the bare metal surface on the above reaction. A low hydrogen to carbon monoxide ratio would probably promote the water-gas shift reaction. On an improperly conditioned catalyst both of these reactions proceed consecutively, the water gas shift reaction initially lagging the methane reaction. Consequently only water and carbon dioxide are produced.

An active Fischer-Tropsch catalyst will ultimately cease synthesizing oil due to the accumulation of heavy waxes on the surface. Revivification is brought about by a low temperature hydrogen activation. Coating of the surface results from the large proportion of the catalyst existing as carbide after continued synthesis. According to the theory, very little chemisorbed hydrogen can exist on the surface in this highly carbidic stage and hence there is formed heavy oils and waxes which cover the catalyst surface. Hydrogen reacts chemically with these heavy waxes in such a way that they are desorbed, thereby leaving a clean surface (9, 10).

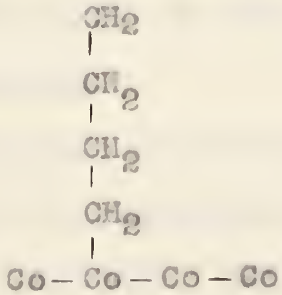
Storch (69) agrees with Craxford that the formation of carbide from carbon monoxide and metal by the conventional reaction is too slow but offers a different explanation for it. He suggested that the presence of hydrogen catalyzes the carbide reaction by forming first an unstable metal hydride. This hydride might cause distortion of the metal lattice to such a degree that upon removal of the hydride the penetration of the lattice by carbon monoxide is enhanced. Removal of the hydride could take place by decomposition or by reaction with neighboring metal carbide or carbon monoxide. The presence of a large amount of hydride would catalyze the ortho-para hydrogen conversions, but as this is known to occur to a very small extent during oil synthesis it was assumed that the amount of hydride necessary to catalyze the carbide reaction was much less than is necessary to promote the slight ortho-para conversion. Furthermore, the presence of hydrogen in the reaction is consistent with the fact that water is the main oxygenated compound produced during synthesis.

Fischer and Pichler (31) have found that the yields obtained from a cobalt-thoria -kieselguhr catalyst can be increased by operating in a pressure range of between five and fifteen atmospheres. Above this pressure yields decrease rapidly. They have suggested that oxygen containing compounds which are formed at pressures greater than fifteen atmospheres probably act as poisons, but at the lower pressure they are hydrogenated and rendered harmless to the synthesis. Storch has suggested that the decrease in activity

is due to corrosion of active catalyst surface by carbonyl formation and by the stronger adsorption of oxygenated organic compounds which are produced in larger amounts at higher pressures. If it is true that corrosion of active catalyst centres occurs at high pressures, it is possible that the observed decrease in the life of the catalyst when operated at high pressures is also due to this effect.

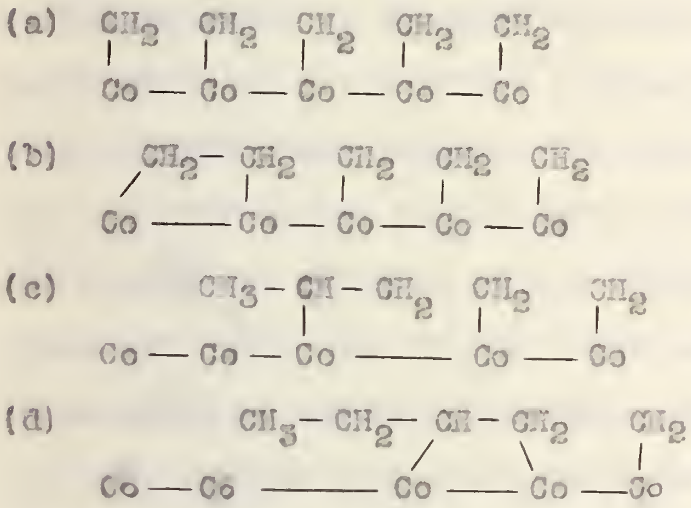
Twigg and Rideal (74) have demonstrated that ethylene could be adsorbed on nickel atoms spaced at their distance of closest packing in the nickel surface. The same is true for cobalt. It is known that this particular packing of the metal atoms occurs during oil synthesis on a Fischer catalyst. Subsequently, Herington (48) showed that on nickel and cobalt catalysts the atomic spacings are such that two point contact of an olefin~~e~~ can be maintained. This led to a different conception of how methylene groups are adsorbed and polymerized on a cobalt surface.

The mechanism whereby a chain of methylene groups are formed by the successive combination of free methylene groups with the groups already attached to the surface is unlikely, as this would imply that the methylene groups are mobile on the surface and that the desorbed olefin~~e~~ must be an α-β unsaturated olefin~~e~~ e.g.



$$\begin{array}{c} CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ Co-Co-Co-Co \end{array}$$

In the light of the probability of dual bonding of the olefins on adjacent metal atoms, the mechanism whereby fragmentation of a giant molecule occurs is less likely than the mechanism which takes this bonding into account e.g.



In (a) the reduction of carbide produces methylene groups. Two of these combine to form C_2H_4 (b) which reacts with an adjacent methylene group to form C_3H_6 (c). Simultaneously a hydrogen atom migrates (d) and two point contact is maintained. This mechanism explains the occurrence of a mono olefin~~e~~ with the double bond in the terminal position and further indicates that ethylene is the only product which is held by all its carbon atoms and also possesses two reactive centres for polymerization. Because of the fact that ethylene is an intermediate for polymerization the yield of ethylene or ethane will be less than the yield of higher homologs.

On the basis of this mechanism an explanation is also offered for the production of oils when ethylene is introduced into the synthesis gas. Ethylene will be adsorbed

on the same metal atom spacing as is in use for oil synthesis, that is, the spacing which corresponds to the closest packing of the atoms. Consequently it enters into reaction on the surface and is incorporated into the oil products.

Myddleton (57) has suggested that perhaps carbon monoxide is adsorbed by dual attachment on adjacent metal atoms of the catalyst surface with simultaneous formation of methylene groups. The methylene groups would give rise to hydrocarbon chains while water would be formed by the subsequent reaction of the adsorbed carbon monoxide with molecular hydrogen. On the other hand if carbon monoxide is adsorbed by single attachment, molecular hydrogen would probably produce methylene groups and carbon dioxide instead of water. The presence of chemisorbed hydrogen would result in the conversion of the methylene groups to methane. As yet experimental evidence has not been offered in support of this theory.

Komarewsky and Riesz (52) suggest that the search for suitable catalysts to produce oils can probably be narrowed down by use of the "complex action" catalyst conception. Two separate influences are present on the catalyst surface, namely, the hydrogenating effect and the polymerization effect. It is the combined effect of these two that influences the reaction. It is assumed that the reaction proceeds by way of the metallic carbide and thus the catalyst must contain a metal capable of forming a carbide, a hydrogenating catalyst to reduce the carbide to methylene groups and a polymerization catalyst to polymerize these

groups. Hence the catalyst must comply with the following conditions:

1. Ability to form a carbide from carbon monoxide
2. Hydrogenating ability
3. Polymerizing ability.

Thus for example, if pure nickel were used as a catalyst, excessive hydrogenation would take place and methane would be produced. Consequently the nickel is carried on kieselguhr to cut down the hydrogenation reaction.

On this basis, the effect of sulphur as already noted, can be explained as well as the effect of introducing ethylene on the catalyst surface. The sulphur probably readily poisons the hydrogenating part of the catalyst whereas the polymerization part is not affected and hence long chain hydrocarbon yields are increased initially at the expense of the lighter hydrocarbon yields. If sufficient sulphur were added, the hydrogenating part of the catalyst would be completely destroyed thereby stopping all reaction. When ethylene is introduced on the catalyst surface it is strongly adsorbed on the surface and being highly reactive enters into reaction with the carbon monoxide and the methylene under the influence of the polymerising part of the catalyst. The hydrogenating influence remains comparatively constant and hence higher yields of oil are obtained.

The increased life and activity of the catalyst in the pressure range of between five and fifteen atmospheres is attributed to the fact that in this pressure range the sensitivity to poisoning of the hydrogenating portion of the

catalyst is reduced. Hence, long periods of catalyst activity might be expected.

Boomer (7) has suggested that the loss of activity on any catalyst might be due to oxidation by water formed in the reaction. There is no evidence of this oxidation, hence if it does occur it is slow and is not affected by a low temperature hydrogen activation at 200°C. At 400°C., however, any oxides would be reduced. Another suggestion offered by Boomer was that formation of stable carbides at operating temperature might occur causing irreversible poisoning. He points out that sulphur and arsenic probably combine chemically to form irreducible residues on the catalyst surface which cannot be reduced even at 400°C. The marked sensitivity of cobalt catalysts to these poisons is probably due to this fact. The sensitivity of the catalyst to high temperatures results from the fact that the catalyst is sintered and the few active centres that might have been present are reduced to insignificant numbers.

Iron catalysts are distinguished sharply from cobalt catalysts by the production of olefins, carbon dioxide, the impossibility of reactivation, the rapid loss of activity at normal pressure and long life at intermediate pressures. It has thus been concluded that the reaction on an iron catalyst is essentially different from that on the cobalt and nickel type of catalysts. The formation of intermediate carbides as a primary step in the synthesis of hydrocarbons seems to be generally accepted.

Smith, Hawk and Golden (67) found that the introduction of ethylene into the synthesis gas over an iron-copper catalyst had no effect on the reaction. No oxygenated products were obtained and the yield of oil was not increased. In addition, much smaller amounts of methane were obtained. They suggested the possibility that intermediate oxygenated compounds were formed and were rapidly decomposed to produce hydrocarbons. The main conclusion, however, was that the reaction was essentially different from that encountered on the cobalt catalysts.

Myddleton (57) has pointed out that according to Craxford's theory the behavior of iron catalysts is anomalous in many ways. Of greatest importance is the fact that during the production of higher hydrocarbons, carbon dioxide is produced exclusively. He suggests that carbon monoxide is adsorbed by single attachment to the iron atoms and not by dual attachment as with cobalt. Molecular hydrogen then produces methylene groups and carbon dioxide. These methylene groups give rise to the hydrocarbons. Dual attachment to adjacent metal atoms as with cobalt is impossible because of the larger atomic spacing in the iron catalyst.

Storch (69) suggests as before, that the formation of hydrides catalyzes the production of carbides on iron catalysts and these act as intermediates in the formation of hydrocarbons. He also points out that at the temperatures employed with iron catalysts the water-gas shift reaction is catalyzed to a very slight degree and thus carbon dioxide must be produced as a primary product.

Recent patents (55) disclose that iron catalysts, "sintered" by reduction at 650 - 850°C. produce iso-paraffins, whereas these are produced in very small amounts on an iron catalyst reduced at 400°C. Storch (69) believes that the sintered catalyst contains no iron oxide whereas those reduced at low temperatures contain significant amounts of iron oxide. Hence, a critical spacing of the iron lattice is obtained by sintering. The spacing between some of the planes containing iron atoms must be sufficiently altered to permit cross linkages to form, so as to produce a large proportion of isoparaffins.

On the basis of the "complex action" conception, the failure of ethylene to take part in the reaction on an iron catalyst, is explained by the fact that it is probably not sufficiently adsorbed on the catalyst and is not available for reaction with carbon monoxide and hydrogen. In the light of the dual bonding of ethylene to adjacent metal atoms on a cobalt catalyst, this failure of ethylene to react would indicate that it is not an intermediate in the reaction and that the atomic spacing of the iron atoms is not such that dual bonding of ethylene can occur.

The most recent work on iron catalysts has been carried out by Pichler (61). He pointed out that all early theories involved the formation of higher carbides during the synthesis and were necessary for the reaction. These higher carbides were probably Fe_2C or compounds even higher in carbon content. In his investigations, however, he showed that these higher carbides decomposed at higher temperatures

(300-400°C.) leaving Fe_3C as the only stable carbide. The most active catalysts were those containing the largest amount of Fe_3C. During the synthesis the decrease in catalyst activity can be attributed to the decrease in the amount of Fe_3C which is paralleled by a corresponding increase in the concentration of Fe_3O_4. An equilibrium or pseudo equilibrium mixture of Fe_3C and Fe_3O_4 probably exists on the catalyst. Thus, when this apparent equilibrium exists on an iron catalyst, there is no rapid drop in activity while with a higher concentration of Fe_3C an initial decrease in activity is observed.

By magnetic measurements, Pichler (61) showed that besides Fe_3C and Fe_2C, a third carbide, richer in carbon was present. Apparently the Fe_3C crystallites are embedded in a phase in which the C:Fe ratio is greater than 2:1. It is evident that this mixture of carbides plays an important part in the reaction mechanism on an iron catalyst.

The catalyst is probably sensitive to high temperatures because at higher temperatures Fe_3C becomes sintered and is inactive insofar as its particular function in the catalyst is concerned.

Pichler (61) suggests that isoparaffins are formed through intermediate higher alcohols, primarily isobutanol. Olefins result from these alcohols and are subsequently hydrogenated to the corresponding iso-paraffins. The combination of these reactions results directly in the formation of isoparaffins, from carbon monoxide and hydrogen.

Koomer (7) has mentioned the possibility of the

water-gas shift reaction occurring on the catalyst.

H_2 + CO + Fe = Fe carbide + H_2O

H_2O + CO = CO_2 + H_2

Fe carbide + H_2 = Fe + CH_2 chain.

The methylene groups which break off while short are not hydrogenated and remain olefinic in character.

Iron catalysts lose activity rapidly at one atmosphere and in this respect Boomer supports the idea that active centres are lost through volatilization as carbonyls. There is no doubt that these carbonyls exist. Poisoning probably occurs in the same manner as on cobalt catalysts.

INDUSTRIAL DEVELOPMENT AND DESIGN

Historical

The first and most intensive laboratory work on the hydrogenation of carbon monoxide was carried out by Fischer, Tropsch, and co-workers at the Kaiser Wilhelm Institute in the Ruhr, Germany. This Institute is supported by the Ruhrchemie A.G., a company jointly owned by approximately 80% of the coal and coal tar producers of the Ruhr.

In 1933, Ruhrchemie A.G. felt that laboratory work had proceeded to such a stage that an experimental plant was possible. Accordingly, the first Fischer-Tropsch industrial plant was constructed at Oberhausen-Holten, Ruhr, Germany, in the same year. This plant had a capacity of 1000 tons per year of primary product or "Kogasin", and was equipped to produce motor fuel and lubricating oils. Synthesis gas, with a hydrogen: carbon monoxide ratio of 2:1, was made from coke and was passed over a nickel-alumina-manganese catalyst supported on kieselguhr at temperatures of 190° C - 210° C and one atmosphere pressure. According to Storch (68), the chief operating difficulties encountered in this first plant were as follows:

1. Too short a catalyst life.
2. A cheaper design was required for the convertors and the sulfur removal plant.

3. An industrial process was needed for the recovery of metals and rare oxides from the exhausted catalysts.
4. The gasoline fraction produced had a poor octane number.
5. A cheaper method of manufacturing the synthesis gas was required.

By 1936 these difficulties had been overcome to such an extent that five plants having a capacity of 145,000 metric tons of primary products annually were in operation in the Ruhr. It is interesting to note that a variety of sources were used for producing the necessary synthesis gas; two plants used coke as a raw material, one used a mixture of coke and coke oven gas, and two gasified brown coal or brown coal briquets.

Production of Kogasin in Germany in 1938 had been raised to 525,000 tons per year by increasing the capacity of existing plants and constructing new plants. About the same time two plants were reported in Japan (68), having an output of 150,000 tons per year, with several new plants under construction. One plant has also been reported in France with a rated capacity of 20,000 tons per year, although it has never achieved this figure. Two smaller experimental plants, of about 150 gallons per day capacity, were erected in Great Britain to test the Fischer-Tropsch synthesis and the Robinson-Bindley process, (a modification of the Fischer-Tropsch).

German plants have been reported to yield a product of which 60% is a gasoline fraction having an octane number of 40, and an appreciable oil fraction which is a high quality diesel fuel. Excellent lubricating oils can be synthesized from the primary product.

Plant Design

The most recent and comprehensive data on industrial designs is that included in the reports by the Combined Intelligence Objectives Sub-Committee (8), obtained in 1945 during their examination of German industrial processes and company documents. Although reports on several plants are available, only one will be presented here in any detail, since other plants conform fairly closely to the same general pattern.

It is of interest to list here the processes developed at the Kaiser Wilhelm Institute and credited (8) to Fischer and his co-workers. The following tabulation summarizes them conveniently:

Table 6

Year	Process	Oper. Press. Atmos.	Catalyst
1922	Synthol-oxygen containing derivatives of hydrocarbons	100	Fe, Co, Ni
1923	Synthane--hydrogenation of Synthol products	---	---
1925	*Benzine, some olefins	1	Fe, Co, Ni
1936	Benzine, little olefins	5 - 20	Fe
1937	Benzine, much olefins	5 - 20	Fe
1938	Solid paraffins, high melting	Over 100	Ru
1941	Iso-paraffins,	Over 100	Ru
1942-43	Naphthenes, aromatics formic acid, fatty acids, alcohols		

Work was also being conducted on other metals as catalysts, since the German supplies of nickel and cobalt were becoming inadequate. The processes most commonly used were those employing cobalt and nickel catalysts in the "atmospheric" and "middle pressure" syntheses.

One of the most complete synthesis plants operating in Germany was situated at Holten-Sterkrade, Ruhr, and was operated by the Ruhr Chemie A.G. In 1945 this plant consisted of:

1. A complete low pressure Fischer-Tropsch unit for the production of benzine and diesel fuel.

*"Benzine" is a term commonly used in Germany to designate a mixture of hydrocarbons boiling in the gasoline range.

2. A complete medium pressure synthesis plant for the manufacture of olefins.

3. A complete lubricating oil plant for synthesizing these oils from olefins.

4. A plant for the manufacture of catalyst for owner's and for licensee's use.

The plant also contained units for the production of nitrogen products, hydrogen, nitrogen and oxygen.

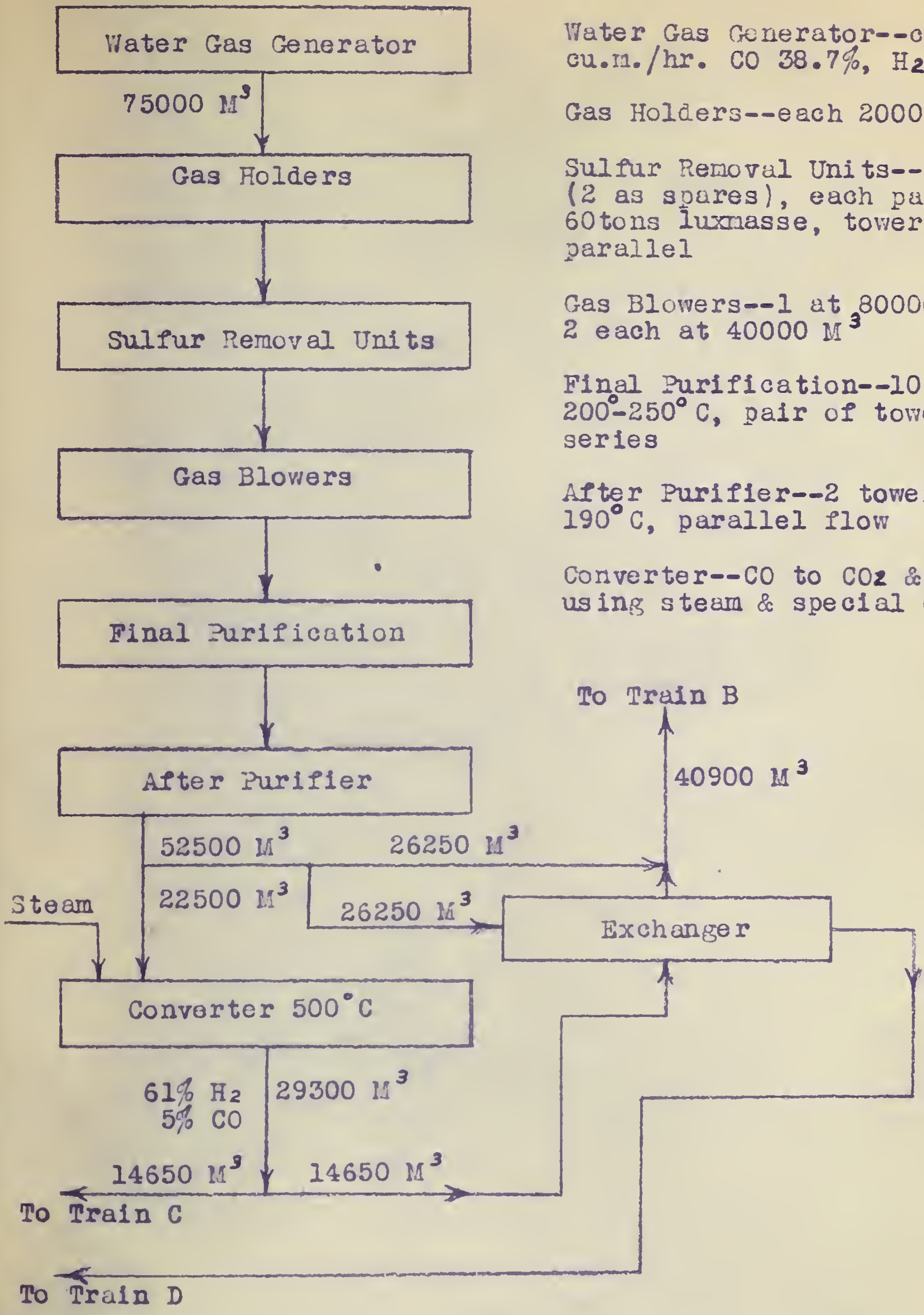
Pilot plant work was also being conducted on the development of the following processes:

1. Benzine with a high octane rating.
2. Iso-paraffins directly from synthesis gas.
3. Isomerization of paraffins.
4. Substitution of cobalt in catalysts by iron and other metals.

The accompanying diagrammatic flow sheets show the various processes used, together with a brief description of the principal pieces of equipment and the hourly flow rates of gases. Sketches of the design of the two types of converters used are also included.

The production of these units is given below:

Paraffin waxes	6000	tons per year
Lubricating oils	6000	" " "
Diesel oil	19,000	" " "
Benzine	25,000	" " "
Propane/Butane	6000	" " "
Total	62,000	tons per year
Catalyst production	900	tons per year



Water Gas Generator--cap.75000 cu.m./hr. CO 38.7%, H_2 48.3%

Gas Holders--each 20000 M^3

Sulfur Removal Units--8 towers (2 as spares), each packed with 60tons luxmasse, towers in parallel

Gas Blowers--1 at 80000 M^3, 2 each at 40000 M^3

Final Purification--10 towers 200°-250° C, pair of towers in series

After Purifier--2 towers at 190° C, parallel flow

Converter--CO to CO_2 & H_2 using steam & special catalyst

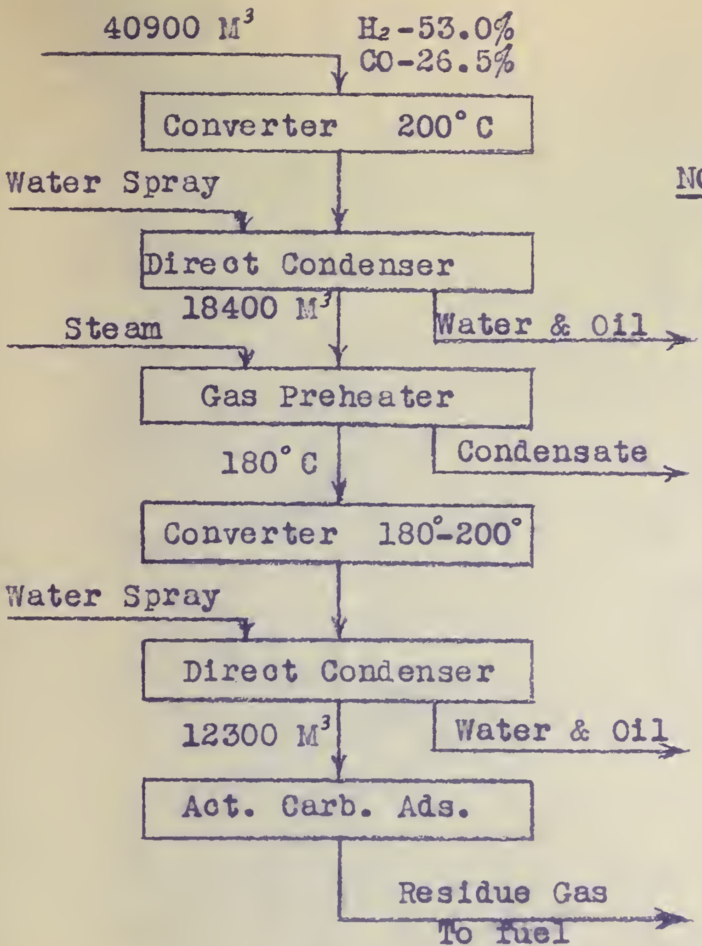
TRAIN A--SYNTHESIS GAS MANUFACTURE

Figure 3

Figure 4

TRAIN B

NORMAL PRESSURE SYNTHESIS

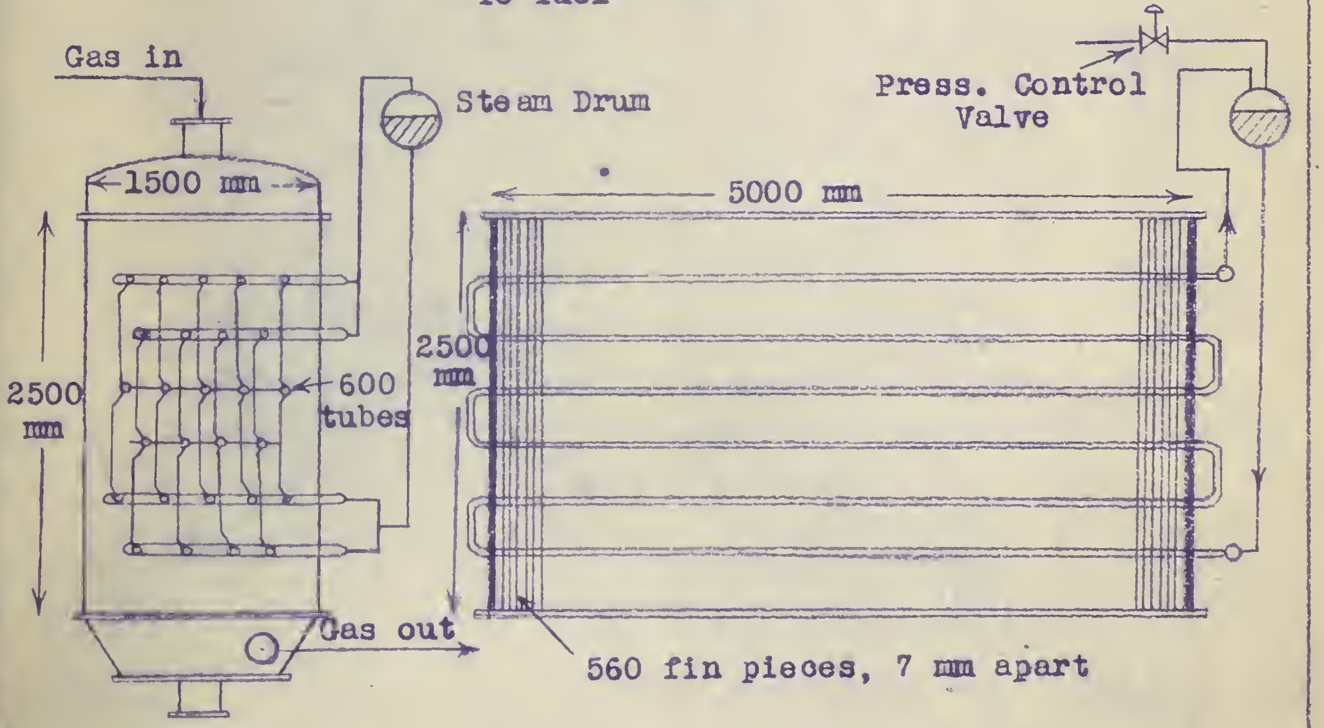


Converters--30% Co, 10% ThO_2 & MgO Catalyst -1°C control

Condensers--Water spray countercurrent to gas flow in vertical tower

Gas Preheaters--Tubular, finned, steam in tubes

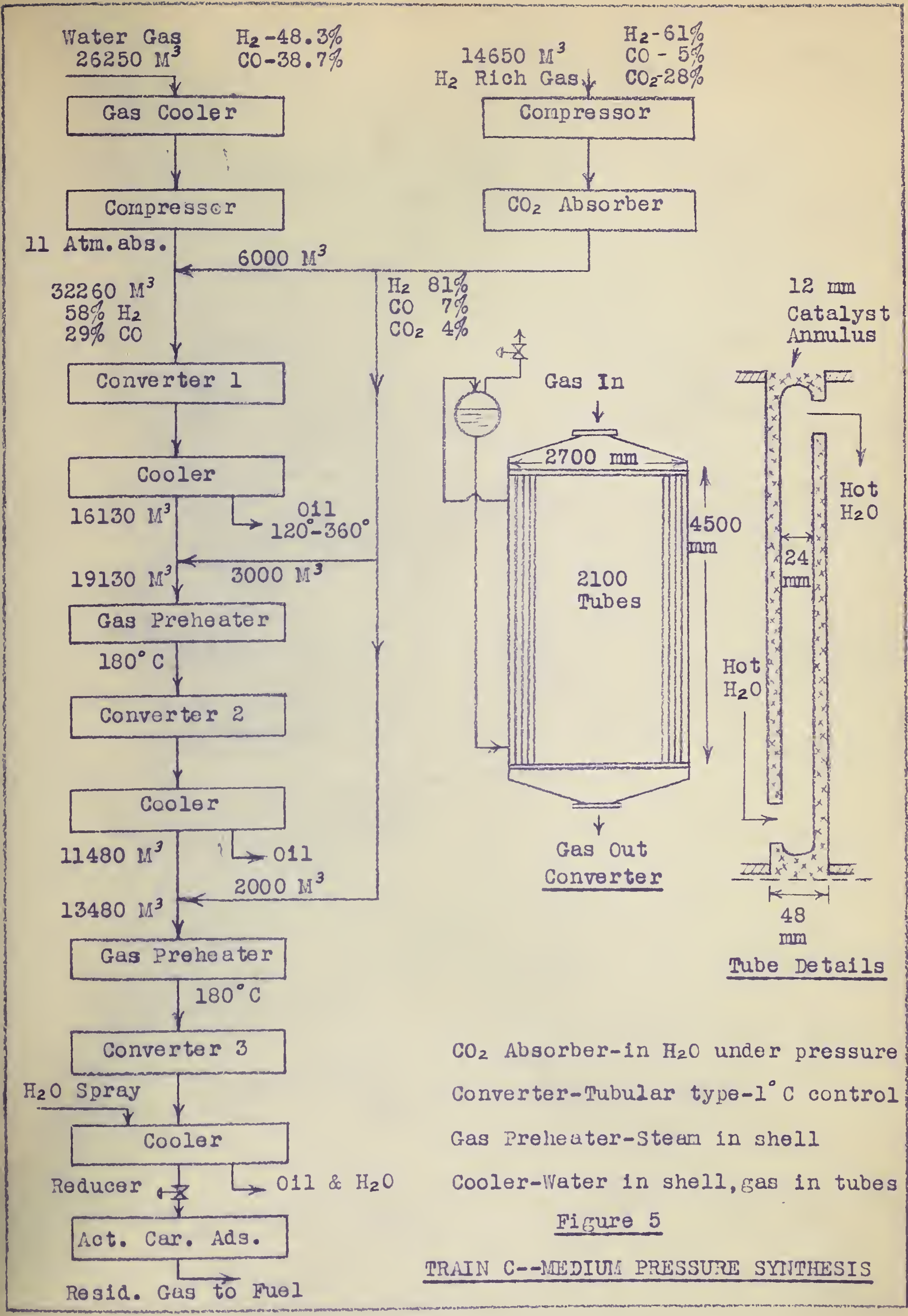
2 Adsorbers--Cyclic operation followed by steam stripping



End View

Side View

Converter Design



CO₂ Absorber-in H₂O under pressure

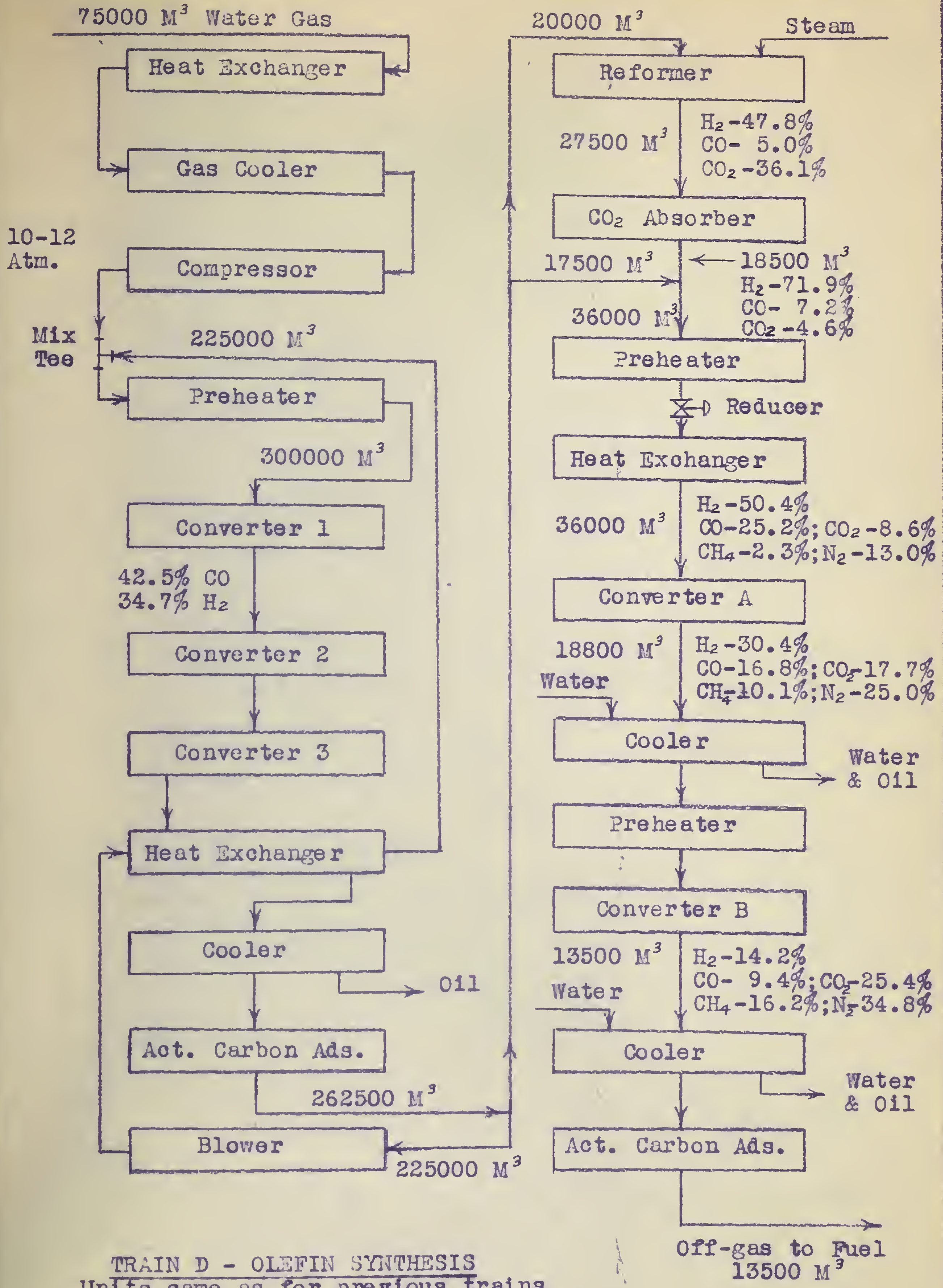
Converter-Tubular type-1° C control

Gas Preheater-Steam in shell

Cooler-Water in shell, gas in tubes

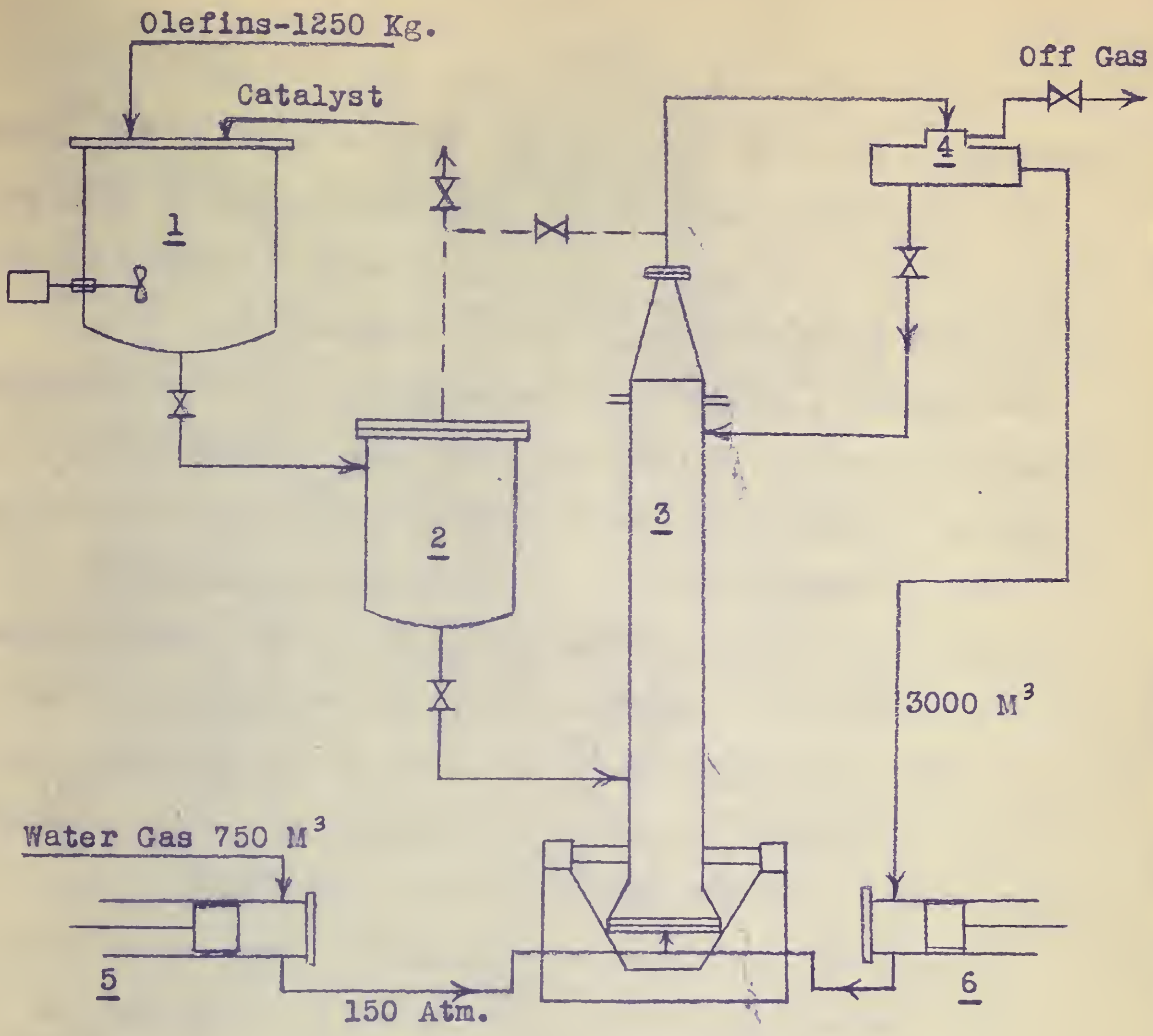
Figure 5

TRAIN C--MEDIUM PRESSURE SYNTHESIS



TRAIN D - OLEFIN SYNTHESIS
Units same as for previous trains

Figure 6



1 Catalyst and Olefin Mixer

2 Charging vessel--pressure equalized after charged from 1.

3 Converter--Bayonet heating and cooling tubes. 125°-145°C

4 Separator--Gas vented from here enough to maintain CO:H ratio

5 Primary Compressor -

6 Recirculating Compressor

Off Gas Composition--CO_2, N_2-20 to 30%; CO-15 to 20% H_2-40 to 50%.

Batch cycle is one hour, half reaction time and other half for charging and discharging.

"OXO" PROCESS

Figure 7

Train A for the manufacture of synthesis gas needs little explanation. The hydrogen rich gas manufactured was used to blend with water gas to give a synthesis gas of the desired composition.

The converters used in the normal or atmospheric pressure synthesis consisted essentially of a complex web of plates with the catalyst being in the intervening spaces. Banks of pipes running through these plates served to control the catalyst temperature. The temperature of the water flowing in the pipes was controlled by the pressure which was maintained on the steam drum. The product from this synthesis was reported to be largely liquid hydrocarbons, with small amounts of gases and solids.

The middle pressure synthesis used a different type of convertor. A double tube contained the catalyst in the annulus with steam in the inner section and steam in the whole of the space between the outer tubes. It was stated that the first converter gave a 50% conversion of the synthesis gas, the second 30%, and the third 21.5% conversion. An iron catalyst had been tested also in this synthesis at 225°C - 240°C, resulting in the production of more unsaturated liquids and less solids and gases than was obtained from the cobalt catalyst.

The olefin synthesis (Figure 6) used a synthesis gas with a hydrogen: carbon monoxide ratio of 1.00:1.23. The first train in this synthesis produced less solid and considerably more unsaturated hydrocarbons than the second

normal pressure train. A space velocity of 80 was maintained and the following yields were reported:

Train 1 --	10	grams/cu.m. of liquefiable gas
	120	grams/cu.m. of liquid products
Train 2 --	30	grams/cu.m. of total products
Total yield	160	grams/cu.m. of liquid and gaseous products

It can be seen that the synthesis gas consisted of three parts recycle gas and one part purified water gas. A slightly higher operating temperature was maintained than in other units, that is 200° C--210° C. The same type of converter was used as in the middle pressure synthesis for the first three units of the train, and the normal pressure type in the last two.

Some special mention of the so-called "OXO" process is necessary, as this was one of the few entirely new German developments. In this process the C_{12}-C_{17} olefins were treated with purified water gas at moderate temperatures and pressures yielding aldehydes in the C_{12}-C_{18} range.

The raw material was straight chain olefins having the double bond situated at the end of the hydrocarbon chain. Such olefins may be obtained from the Fischer-Tropsch primary product or from Dubbs cracking of the C_{20}-C_{40} paraffins. The aldehydes formed were hydrogenated to fatty alcohols which were sulfonated to yield excellent detergents.

The process was carried out batchwise, at a pressure of 150 atmospheres, with the reaction temperatures

varying from 125° C to 145° C. A standard cobalt catalyst was ground to 200 mesh and suspended in the olefin charge. The water gas used had a composition of 38% carbon monoxide, 48-49% hydrogen, with the remainder being carbon dioxide and nitrogen. The hydrogenation of the crude product was carried out at 180 atmospheres pressure and 180° C, using the same catalyst and the same type of equipment. The crude alcohols were then purified by vacuum distillation.

Some of the most reliable data concerning catalyst life comes from the Fischer-Tropsch plant at Bergkamen, Germany. The synthesis was operated in two stages. The freshly reduced catalyst was first put in stage II at 180° C for a period of 2-3 months. The contraction here was approximately 25%. The catalyst was then transferred to stage I at 190° - 192° for a further 5-6 months, thus giving a total catalyst life of 8-8 1/2 months. When contractions tended to drop to some predetermined level a reactivation with pure hydrogen was carried out for 24 hours at a temperature of 195° C. At times the catalyst activity dropped due to accumulations of heavy waxes on the catalyst surface, in which case an extraction with benzine was necessary. The oven was isolated and benzine of a 160° C - 220° C boiling range was allowed to trickle over the catalyst at 120° - 150° C. The benzine was then distilled and the distillate returned to the oven top until the extract no longer contained wax.

The complete extraction required 1 to 1 1/2 days. At this plant the catalyst with the longest life was reported to have been given 6 extractions and 8 reactivations during this time.

Synthesis Gas Manufacture

Considerable progress was also made in Germany in the production of synthesis gas. Some new designs have been reported and considerable data on the respective merits of different types of continuous gasification units have been obtained. A very brief discussion of these methods, as used in Europe, is given below.

Winkler generator--These generators operate on brown coal briquets, lignite, coal or semi-coke. The fuel is subjected to a continuous blast of gas containing one volume of oxygen (as oxygen or air), and 2 volumes of steam at 375° C. The fuel is fed into the generator by a hopper at the bottom of the fuel bed. This bed is maintained at a thickness of about 5 feet, and is kept in continuous agitation by the gas blast. The sintered ash particles settle on to a grate, where, after being cooled by the incoming gases, they are moved to a discharge port by a rotating brass water-cooled rabble. The synthesis gas produced is cooled and subjected to dust removal operations. The product has a composition similar to water gas but with a carbon dioxide content of 15-20%. If air is used the gas will also contain about 20% of inert

gases. The Winkler generator can thus operate on a variety of fuels, and has a capacity almost five times that of the old water gas machines.

Didier Generator--This unit is a combination vertical retort and water gas generator, operating on 1/4" - 1" bituminous coal or lignite briquets. It has six superposed zones; 1. drying 2. predistillation 3. carbonization at high temperatures 4. conversion of gaseous hydrocarbons 5. formation of water gas 6. cooling of coke. Enough methane is produced in the carbonization zone so that reaction with steam will give the final gas product a carbon monoxide; hydrogen ratio of 1:2. Only enough coke is produced in the process to manufacture sufficient gas to heat the carbonization chamber. Steam at 400° C - 500° C is consumed in the process. The final gas product has a carbon monoxide and hydrogen content of 87% with the remainder carbon dioxide. When using lignite the thermal efficiency is stated to be 75.7%.

Pintsch-Hillibrand generator--This machine is similar to the Didier generator. A mixture of preheated steam, carbonization gas and some synthesis gas flows countercurrent to coal briquets.

Lurgi Pressure generator--Gasification is carried out in a tower under 20 atmospheres pressure, using almost any solid fuel and a mixture of steam and oxygen. The higher pressures favor the production of carbon dioxide and methane, but it is claimed that by adding carbon dioxide to the oxygen-steam mixture a gas with a hydrogen: carbon monoxide ratio of 2:1

can be obtained. This generator is considered to have great possibilities since it has almost three times the capacity of any other type.

Schmalfeldt-Wintershall Process--This process combines drying and gasification by passing the newly produced synthesis gas over the raw coal, thereby cooling it, and drying and partially gasifying the coal. A mixture of steam and oxygen is fed into the unit and coal dust is gasified in the down flowing stream. Conversion in the first chamber is kept down to 50% to avoid excessive temperatures. Some of the synthesis gas produced is reheated and recycled to maintain continuity of gasification. A second gasifier serves to give the desired hydrogen:carbon monoxide ratio. The unit consists of the following items; 1. Preheater 2. Gasifier I 3. Gasifier II 4. Drying pipe 5. Dust catcher 6. Scrubber 7. Blower. It has been found that the composition of the gas produced is not constant, and large quantities of heat are lost. However, it was felt that the German designed unit was faulty in many respects, and that the process could be made one of the most economical of its type. It was also noted that the gas produced contained 5% of benzol, which constitutes a very valuable by-product.

Other methods of synthesis gas production have also been reported, some only in the experimental stages. One German plant carried out a cracking process on Fischer-Tropsch tail gas with a mixture of oxygen and steam. However, at the war's end, conclusive data had not been obtained on

this method. Partial oxidation of methane also offers a very economical source of carbon monoxide and hydrogen. However, no industrial units have been reported as yet, at least, not for the production of Fischer-Tropsch synthesis gas.

Dolch (11), in his summary of gasification processes, concludes that the methods using oxygen-steam mixtures are superior to those which involve the separate gasification of a part of the fuel. It was also stated that vertical ovens operating at one atmosphere with oxygen-steam mixtures produce less methane and consume less oxygen than other types.

Catalyst Manufacture

The manufacture and regeneration of the Fischer-Tropsch catalyst, and the removal of sulfur from the synthesis gas, are probably the two most important single factors affecting plant operation. In the case of catalyst manufacture, a staff of trained chemists and the most modern control equipment is necessary to ensure an active product. Therefore a considerable portion of the costs must be assigned to this phase of the process.

A complete report (8) has been obtained on the method used at the Carrieres-Kuhlman plant, Harnes, France. The raw materials were pure cobalt metal, magnesium oxide, thorium oxide, and kieselguhr. The catalyst in the unreduced form had a composition of cobalt 13%, magnesium oxide 1.8%, thorium oxide 0.9%, and kieselguhr 79.3%.

The specifications for the raw materials were rigid.

The cobalt metal was required to have a purity of 99% with the remaining 1% being copper and nickel. The thorium oxide had a calcium oxide content of less than 0.2% and contained no traces of lead or phosphorus. The kieselguhr on analysis showed a silica content of over 92%. None of the materials contained calcium oxide or iron since these were considered poisons.

The equipment consisted of three large tanks, mechanically agitated, so arranged that the first two could be quickly and simultaneously dumped into the third. Into the first tank was put the cobalt, magnesium oxide, and thorium oxide, and the necessary amount of 36°Be nitric acid, (made from distilled water). In this tank the metals went into solution as nitrates. The second tank contained distilled water and the required amount of a 10% sodium carbonate solution. The first and second tanks were then dumped simultaneously into the third where the resulting solution was agitated at a temperature of 100° C. A pH of 7.2 was maintained in order to prevent the formation of bicarbonates, which, it was claimed, destroyed the efficiency of the kieselguhr as a supporting agent. The reactions which occurred here gave a mixture of cobalt hydroxide, magnesium carbonate, and thorium carbonate. The kieselguhr was next added and the solution thoroughly stirred.

The slurry was next sent through a series of filtrations and washings with distilled water, which are listed briefly below:

1. A fast filtration in a plate type filter press.
2. A washing in a horizontal mixing tank with a screw type agitator.
3. A filtration in an Oliver rotary type filter.
4. Water content reduced to 60% in an extruding type press.
5. Dried to 6-8% water content on a moving belt in a steam heated drier maintained at 120° C.

The catalyst was then sized on vibrating screens. The fines so removed were returned to the horizontal mixing drum, while the particles of optimum size were recovered for reduction. These pellets were placed on a screen tray in a special container having conical ends connected to a closed hydrogen circuit. The hydrogen was preheated to 350° C - 400° C before entering the container. The exit gas was dried by passing through water-cooled coils, ammonia cooled coils, and finally silica gel, and then returned for recirculation. The reduced catalyst contained cobalt, cobalt oxide (ratio 7:3), magnesium oxide, thorium oxide, and kieselguhr. When reduction was complete the reactor was cooled and filled with carbon dioxide and the catalyst was then transferred to a closed bucket container, still in a carbon dioxide atmosphere.

The spent catalyst was regenerated by a similar process. The metals were taken into solution as nitrates, and the solution filtered. The cake was washed and the kieselguhr discarded. The magnesium and thorium were separated from the cobalt and any calcium by precipitation as carbonates

at a pH of 4.2. The calcium was removed from the cobalt by precipitation as its fluoride, and the cobalt nitrate solution was ready to use as part of the new catalyst.

The cake containing magnesium carbonate, thorium carbonate, sodium sulfate, and ferric hydroxide was nitrated and then treated with sodium hydroxide solution. The magnesium and iron were precipitated as hydroxides, while a double salt of sodium and thorium was formed which remained in solution. This solution was heated after removal of the magnesium hydroxide and ferric hydroxide, causing a precipitate of thorium hydroxide to form. This was recovered and used in the preparation of new catalyst. The magnesium was discarded since its value did not warrant any attempts at recovery.

Sulfur Removal

The problem of sulfur removal from the synthesis gas presents no difficulties. It is felt that sufficient detail has been given earlier in this article on industrial methods of sulfur removal. It is only necessary to state that standard methods are used which are not unique for this process.

Summary

The Fischer-Tropsch plants which have been in operation to the present time can doubtless be improved in almost every aspect. A successful industrial design must solve several problems which are peculiar to this synthesis. These difficulties are briefly listed below:

1. Heat exchange--Since the Fischer-Tropsch

catalysts are sensitive to temperature, and since the reaction is highly exothermic, an efficient means of heat transfer must be devised. The nature of the catalyst makes it a poor heat conductor, and the low space velocities which must now be used result in inefficient heat transfer. Hence, thin layers of catalyst and large amounts of steel are required in any design.

2. Catalysts--More active catalysts will result in higher space velocities, and might greatly simplify the heat transfer problem. Yields of the order of 70% of the theoretical are the maximum which it has been found practical to maintain in actual operation, and more than one stage is necessary to achieve this result.

3. Laboratory procedures--As more fundamental data is available, more economical design and operation will be possible for industrial plants.

It may be of interest to mention here the possibility of a fluid catalytic unit as applied to the Fischer-Tropsch synthesis. It has been rumored that this possibility is being investigated, and apparently with encouraging results. Such a converter is stated to give high yields, and to have a notably larger capacity than the fixed-bed type. Much greater space velocities are used and slightly higher temperatures and pressures than in other modifications. The catalyst is a finely pelleted iron. However, no data has been published as yet concerning the performance of such a unit.

ECONOMICS

Since May, 1945, many reports have been received on German synthetic fuel processes but no cost data of any value has been published. In any case, it is probable that such data would be valueless considering the abnormal economic conditions which existed in Germany during the war years. Therefore, apart from a very small amount published previous to 1939, there is no specific information available which would in any way indicate the actual costs of an industrial Fischer-Tropsch plant on this continent. However, several complete estimates of costs have been made by responsible men, and it is these estimates which furnish the most reliable picture of the present economic status of this process.

It may be of interest to include here a brief discussion of the situation with regard to raw materials.

As has been mentioned previously, the crude petroleum reserves on this continent are being rapidly depleted. Duce (77) states that the United States has been using 7% annually of its known oil reserves, while 6% is the figure given for Canada. In the past several years, the new reserves found have fallen considerably short of equalling the amount consumed. Further, it was stated that due to the intensive oil exploration program which has been carried out, the prospects for new fields on the North American continent are dim, especially in comparison to other parts of the world

which have not been so extensively exploited. Therefore, although petroleum production will continue for a long time, it will not be many years before it fails to meet the ever-increasing demand. In this case, a supplemental source of liquid fuels must be sought, either from such materials as oil shales and tar sands, or from synthetic processes such as the Fischer-Tropsch and Bergius.

The reserves of oil shales and tar sands are limited in extent, and cannot be expected to yield more than a fraction of the required petroleum. Further, in many respects the recovery of oil from these sources presents a serious economic problem. In fact, coal is almost the only source of fuel which can be considered inexhaustible from a practical point of view.

It would appear, then, that from the long range view point those processes which can use coal as a starting material are the most attractive. It is true that at present they cannot compete economically with those utilizing crude petroleum, but then they have not been developed to such a degree of technical perfection. The Fischer-Tropsch process has the added advantage of operating on natural gas even more economically than on coal. From this starting point it is estimated that the process is financially attractive even at the present time.

It is known that the natural gas reserves of this continent are very large. However, if all the gasoline consumed in the United States were to be made from natural gas, it has been stated that the known reserves would be ex-

hausted in five years. Hence, the Fischer-Tropsch process operating on natural gas can only be considered as a supplemental means of production of synthetic fuel. Further, the quantities of natural gas which can be spared for manufacturing gasoline will fall far short of that which could be used profitably. Natural gas is recognized as a valuable domestic fuel, and thus wherever possible it will be conserved for this purpose.

Consideration of the coal reserves on the North American continent presents a somewhat different picture. Coal, estimated as known mineable reserves, totals some 4000 billion tons, as compared to a reserve of 3 billion tons for natural gas. These figures take more meaning when it is stated (77) that the United States contains 51.9% and Canada 16.7%, of the known coal deposits of the world. The following tabulation conveniently summarizes the raw materials available and the potential yields which these reserves represent.

Table 7

	Hydrogenation Coal	Fischer-Tropsch Coal	Oil Shale	Tar Sands	Natural Gas
Total Reserves: Billions of Tons of Source Material	4000	4000	400	500	3
% of Reserves Practical for Exploitation	26	100	?	1	10-25
Potential Yield: Billions of bbls. Gasoline	1000	6000	50	2	2-4

Note: The potential yield from known crude petroleum reserves is estimated to be 10 billion bbls. of gasoline.

Fairly detailed cost estimates have been prepared (77), and it is interesting to note the wide variation in the final results which have been arrived at by various methods. F. Denig, of Koppers Company, has prepared a cost estimate based on known pre-war German experience, but adapted to meet existing American conditions. The figures given are based on the assumption of capacity operation for 330 days a year, and include fixed charges but exclude profits.

There are two steps in the Fischer-Tropsch process, the manufacture of synthesis gas, and the conversion of this gas into the synthetic primary product. The synthesis gas may be made from coke, coal or natural gas. Estimates of the production costs for each of these raw materials are given below as cents per gallon of primary product.

From Coke

1.	Water gas	(a)	Coke	6.69
		(b)	Labor	0.74
		(c)	Capital cost	1.05
				8.48
2.	Conversion to Synthesis gas			0.38
3.	Purification			1.48
4.	Compression			1.90
	Total for synthesis gas			12.24

From Sub-Bituminous Coal (or lignite etc.)

1.	Coal	1.47
2.	Labor	1.00
3.	Capital Cost	1.40
4.	Purification	1.48
5.	Compression	1.90
	Total for synthesis gas	7.25

This assumes coal available at $1.00 per ton.

From Natural Gas--using the partial oxidation process

1.	Natural gas (@ 5¢ per 1000 cu. ft.)	1.16
2.	Power (for oxygen production)	1.34
3.	Coke	0.42
4.	Water, etc.	0.48
5.	Labor	0.53
6.	Compression	1.48
7.	Capital cost and maintenance (17%)	1.22
	Total for synthesis gas	6.63

This assumes that it requires approximately 250 cu. ft. of natural gas to yield one gallon of primary product.

The costs of the primary product include converters and cracking equipment for transforming these products to a high-octane gasoline. Neither steam nor power is included, since steam is manufactured in the process. No credit is taken for cracking by-products except for the propane and butane produced.

Cost of converting synthesis gas into primary product.

1. Operating cost

(a) Power	0.30	cents/gal.	primary	product	
(b) Water	0.02	"	"	"	"
(c) Labor	0.80	"	"	"	"
(d) Supervision	0.28	"	"	"	"
(e) Miscellaneous	0.15	"	"	"	"
(f) Catalyst regeneration	1.57	"	"	"	"
Total gross operating cost	3.12				
Credit for steam	0.53				
Net operating cost	2.59				
2. Capital cost 17%	3.76				
Total cost	6.35				

These costs are based on a plant making 2424 bbls. per day of primary product. After refining and cracking this will yield 1940 bbls. per day of gasoline. By assuming that the plant is operated to produce not only gasoline but waxes, diesel oil etc., and by taking credits for cracking gases, tail gas etc. in a system of joint accounting for products and by-products, the costs can be materially reduced. Denig also stresses that costs given here can doubtless be lowered by technical and engineering improvements.

These costs as estimated are summarized in the following table:

Raw Material	Cost of syn. gas for 1 gal. product	Total cost of 1 gal. primary product	Total cost of 1 gal. gasoline
Coke	12.3	18.6	24.4
Sub-bituminous coal	7.3	13.7	18.2
Natural gas	6.6	13.0	17.4

Another set of costs were compiled by Russell (77) of the Standard Oil Development Co. These estimates include figures on the amount of coal or gas necessary to produce one bbl. of gasoline by the various processes. The fuel to produce the necessary power, steam etc. is included in the total as given below:

Hydrogenation of bituminous coal-1020 lbs./bbl. gasoline
Fischer-Tropsch (coal) -1360 " " "
Fischer-Tropsch (gas-European design) - 505 " " "
Fischer-Tropsch (gas-American design) - 440 " " "
Average U. S. refinery (crude oil) - 655 " " "
Modern cracking refinery - 373 " " "

The Fischer-Tropsch design using coal is based on the method of converting coal to coke, and the latter to water gas in the standard water gas generator. All the figures given may have some basis in actual industrial practice except for the proposed American Fischer-Tropsch design for natural gas.

For a large plant, of the order of 30,000 bbls. gasoline per day, Russell gives the following overall cost figures:

Coal hydrogenation	15.5¢/gal.
Fischer-Tropsch (coal)	19.2¢/gal.
Fischer-Tropsch (gas)	4.8¢/gal.
Present day refinery (Crude oil at $1.20 per bbl.)	5.3¢/gal.

For smaller plants of the order of 3000 bbls./day the estimated costs per bbl. of gasoline are as follows:

Coal hydrogenation	22.6¢/gal.
Fischer-Tropsch (European coal design)	19.2 " "
Fischer-Tropsch (European gas design)	8.8 " "
Oil refinery (crude at $1.20 bbl.	5.3 " "
Oil refinery (crude at $2.00 bbl.	8.5 " "

All the above figures include overhead and 10% for depreciation besides the regular operating and capital costs. It is assumed that a gasoline of 70 octane number will be produced.

Various estimates have been presented as to the amounts of steel which would be required for the construction of Fischer-Tropsch plants. These estimates vary from 8.9 to 14.3 tons per daily barrel of gasoline, Russell presenting the lower figure and Denig favoring the higher. In plants using continuous gasification of coal, it is estimated that these figures may be as much as ten times too high. Steel requirements then would be of the same order as those for a modern petroleum refinery. Boomer (7) states that a Fischer-Tropsch plant using natural gas would probably require about the same amount of steel as a present day oil refinery, and possibly even less.

Examination of the detailed data given by

Russell for the Fischer-Tropsch process shows that a very large proportion of investment and operating costs is assigned to the production of synthesis gas. In fact, the greatly decreased costs attributed to the process using natural gas rather than coal, obviously depend on this one factor. No mention is made of direct gasification of coal such as was considered by Denig in his estimates, and it is thus probable that Russell's figure for gasoline production from coal by the Fischer-Tropsch process should be considered as a maximum.

Many other authorities have ventured cost estimates for the production of synthetic gasoline by various methods. Boomer (7) has summarized this data very well, and the figures he proposes as the most reasonable appear to agree very well with the opinions gathered from many other responsible sources. This information as summarized below can then be accepted as an authorative cross-section of present day opinions on the economics of various synthetic fuel processes.

1. Coal hydrogenation--A production cost of 15 - 23 cents per gallon of gasoline, with the lower figure the more acceptable. The process has good possibilities for fuel oil production from cheap sub-bituminous coals, with the cost of the final product estimated from $1.20 - $1.65 per bbl.

2. Oil shales and tar sands--These are described

as marginal processes at best at the present time.

3. Fischer-Tropsch--Coke at $5.00 per ton would give a production cost of $6.00 - $8.00 per bbl. gasoline. (14¢-18¢ per Imp. gal.) Coal at $2.50 per ton under a continuous gasification process is estimated to give a maximum cost of $3.75 - $4.00 per bbl. gasoline (11 - 12¢ per Imp. gal.) and coal at $1.00 per ton a cost of $2.50 - $3.00 per bbl. (7 - 9¢ per Imp. gal). From natural gas the cost is estimated at $1.00 - $1.25 per bbl. (3 - 4¢ per Imp. gal.) These figures include depreciation but allow no profit. Boomer states that natural gas at 5 - 10¢ per thousand cubic feet is now considered competitive with petroleum as a source of gasoline. Also it is further stated that coal at 90¢ per ton and natural gas at 12¢ per thousand cubic feet could successfully compete with crude petroleum at $1.50 per barrel.

It has been predicted that the first Fischer-Tropsch plants will be constructed by private industry to operate on natural gas, and the experience thus gained will be applied to units utilizing low-grade coal as a raw material. Government research then would be concentrated on processes for the continuous gasification of low rank coals, and the general processes for direct hydrogenation of coal.

The position of Canada, and Alberta in particular, with respect to future possibilities for the production of synthetic fuels may now be considered. Since

Alberta contains nearly all of the Canadian deposits of natural gas and coal it is of interest to investigate the resources of this province only.

According to Beach (5), the known reserves of natural gas in Alberta appear to be sufficient only for domestic use, especially as the facilities available are expanded, with a corresponding increase in consumption. However, Alberta, particularly the northern section, is relatively virgin territory from the view point of oil and gas exploration. It is known that gas fields exist in the general areas of the Peace and Athabasca valleys, but the extent of these fields is entirely unknown. After further exploration has disclosed new oil or gas fields, it is possible that Alberta will have an excess of natural gas over that which can be used domestically. If this proves to be the case, which is not unlikely, then this province would be particularly suited for the establishment of Fischer-Tropsch plants.

In respect to coal reserves, Alberta is very well supplied. Large deposits of bituminous and subbituminous coals are known. The total reserves have been estimated at 900 billion tons, although many authorities consider this figure a maximum. Even so, it presents a tremendous incentive for the development of processes which can use coal of this type as a source material. Alberta has sufficient high grade coal for domestic purposes so that it has not been found profitable, except

in a few localized cases, to mine any of the large deposits of low grade sub-bituminous coals. The Fischer-Tropsch process is suited to the use of any type of coal, therefore, the cheaper varieties are, of course, the most economical. It is highly probable that beds could be found where low grade coal could be produced in large quantities and at low cost (by strip mining, for example.) In such a case, the construction of a Fischer-Tropsch plant would merit very serious consideration.

It is, of course, assumed that a continuous gasification process would be used in such a plant. Unfortunately, there has been no industrial experience with such units on this continent, and only European designs are available from which to draw conclusions. However, German practice has shown definitely that where it is possible to obtain a cheap coal the continuous process is very superior to the old alternating water gas process using coke, particularly from the economic point of view. Further, it is felt that German units have not done full justice to the possibilities of the process, and have been guilty of faulty engineering practice in the design. It is suggested that research on this aspect of the Fischer-Tropsch process, viz: the production of synthesis gas from coal, may alone be responsible for placing this method on a competitive basis.

In conclusion, it may be stated that by utilizing knowledge gained from German plants, and by further developments on this continent in the technique of manufacturing synthesis gas and obtaining from it a maximum yield of hydrocarbons, the Fischer-Tropsch process can be made to play a very important part in the maintenance of a sufficient supply of liquid fuels for all needs. Further, the Fischer-Tropsch process can be made to yield many valuable chemicals, either as by-products of gasoline manufacture, or from a process operated specifically for chemical production.

Alberta, with its vast resources of coal, and probably natural gas as well, for which no satisfactory use has yet been found, is in a very advantageous position to exploit these processes to the fullest extent.

It would appear at this time that an industrial process of such great promise as the Fischer-Tropsch synthesis is deserving of the most careful consideration, both by private industries and by governmental departments.

EXPERIMENTAL EQUIPMENT

A detailed description of the apparatus employed in these investigations has been given in a previous report (12). A few minor changes were made. The general flow sheet (Figure 3) affords a picture of the overall process.

Referring to the general flow sheet (Figure 8) the following parts have been labelled:

A. - water seal type gasholder, capacity - 10 cubic feet

B. - 220 volt multiple electric furnace

C_1 and C_2 - caustic scrubbers containing 25% NaOH

D. - water seal type gasholder for synthesis gas, capacity - 5 cubic feet

E. - Standard compressed air receiver for high pressure synthesis gas storage, capacity - 6 cubic feet, diameter - 15 inches, height - 60 inches

F_2 - alumina drier - diameter-2 inches, height - 24 inches

F_1 - copper-zinc oxide purifier, diameter - 2 inches, height - 24 inches

G. - control needle valve

H. - reaction chamber of converter

I. - jacket containing heating fluid

J. - compresser - single acting; piston diameter-1-1/4 inches; stroke - 2 inches; external packed gland; poppet type valves; lubricated by automatic oil pump; belt driven by 1/2 h.p. 1700 r.p.m. induction motor

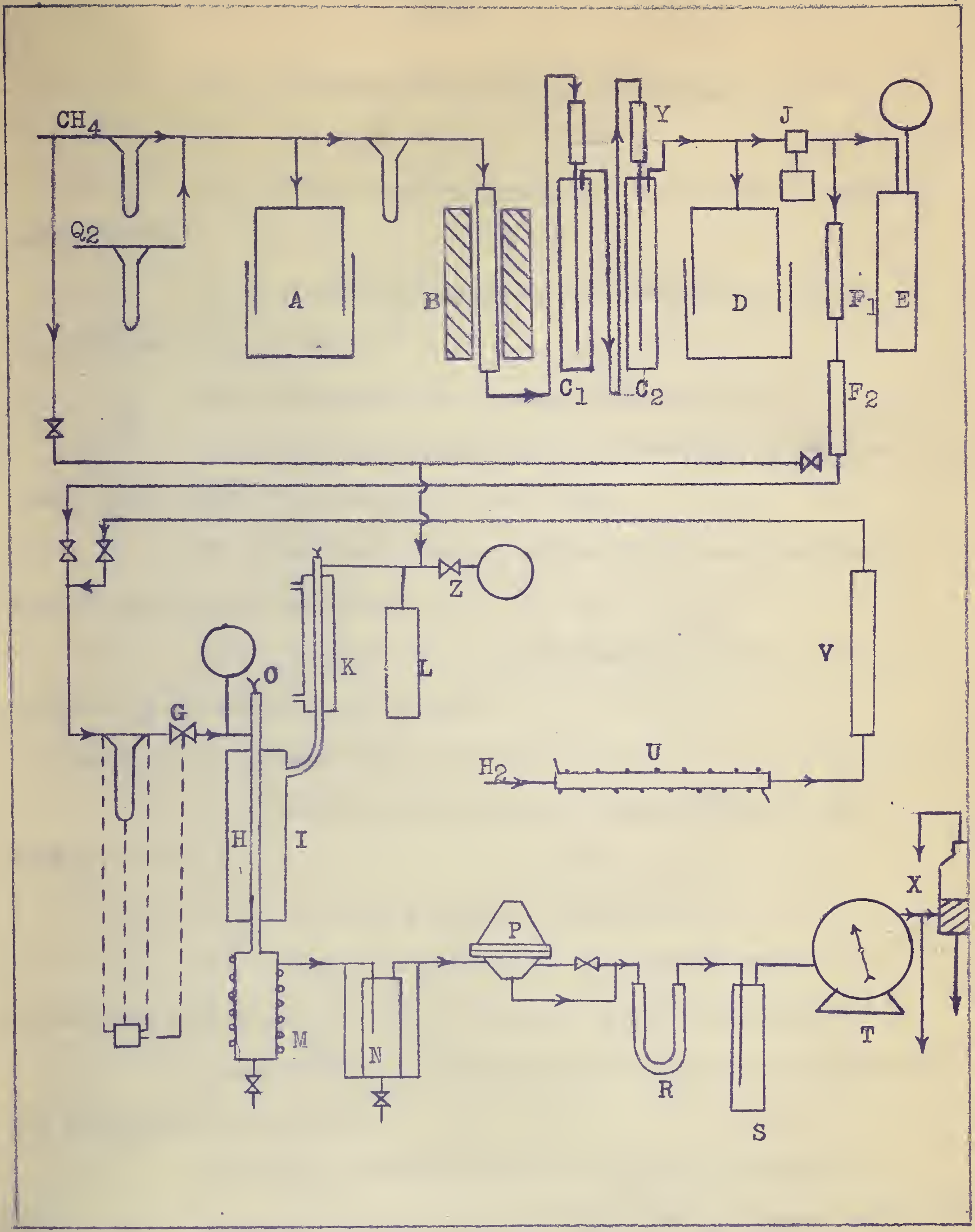


FIGURE 8 - GENERAL FLOW SHEET FOR TESTING OF FISCHER TROPSCH CATALYSTS

K. - water cooled reflux condenser

L. - ballast chamber

M. - steam heated catch pot for product boiling above 100°C.

N. - water cooled catch pot for product boiling between 0°C. - 100°C.

O. - thermocouple - copper-constantan

P. - Cash reducing valve - standard Cash model 1935, size 1/2", "vulcanized fibre" seat

R. - Schwartz ground glass stoppered U-tubes containing calcium chloride

S. - fritted glass type washing bottle (500c.c.) containing approximately 5N.KOH

T. - precision wet test meter

U. - furnace containing metallic copper (250 - 300°C.)

V. - activated charcoal scrubber

X. - continuous gravity type gas sampler - containing 10% Na_2SO_4 and 10% H_2SO_4 as confining fluid

Some additions and some alterations to the existing equipment were made.

Another caustic scrubber (C_2) was placed in series with the existing scrubber to definitely insure the complete removal of carbon dioxide and hydrogen sulfide from the synthesis gas. In addition, an overflow reservoir (Y) was added on each scrubber so that caustic would not run into the gas line in case the scrubbers were plugged.

As a further precaution against the possibility

of poisons being in the synthesis gas a combined zinc oxide-copper purifier was installed in series with, and immediately before the alumina drier. The drier was fabricated of 2" standard iron pipe, 24" long. It was packed one-third full with copper strand and the remainder with zinc oxide pellets. This unit was covered with a layer of asbestos paper and wound with thirty feet of electric resistance wire. The entire assembly was encased in porous asbestos insulation. During operation, the purifier was kept at a temperature of 250 - 300°C. The copper removes any remaining oxygen in the synthesis gas and the zinc oxide pellets remove any remaining sulfur.

Temperature control in the converters was maintained by varying the pressure of an inert gas (methane) above the heating fluid in the jacket surrounding the catalyst column. The pressure in the jackets was indicated by a Bourdon type gauge, range 30"Hg vac. to 60 psi. For reduction purposes however, as much as 120 pounds pressure had to be applied above the fluid to obtain a temperature of 380oC. Hence some other provision for reading these pressures had to be installed.

One-quarter inch brass globe valves (Z) were installed at the inlet to the pressure gauges. At the inlet to the common header carrying the gas to the jackets a Bourdon type gauge, range 0-200 psi., was installed. Thus when normal operation was in progress, and relatively small pressures were required above the heating fluid, the 60 pound gauges were put into the system by opening the one-quarter

inch brass globe valves. On the other hand, when high pressures were required (as for reduction) the quarter inch valves were closed, isolating the 60 pound gauges and allowing the pressure to be registered on the Bourdon gauge, range 0-200psi., at the inlet to the gas header.

An iron-constantan thermocouple line, common to all the converters, was installed and led into the main switch board onto a double throw switch. Temperatures above 300°C. on any of the converters could be obtained by simply attaching a thermocouple from the desired section of the converter to the main line. For temperatures below 300°C., the existing copper-constantan thermocouple line was employed. Since it was very seldom that more than two converters were over at this high temperature at the same time, both temperatures could be obtained readily by use of the double throw switch.

The pellets in the catalyst column were supported from below by a fine wire screen welded to the top of a 3/8" length of pipe which screwed into the bottom of the tube. The length of the catalyst bed could be varied within certain limits by altering the length of the supporting pipe. It was desired to shorten the catalyst column to insure more uniform heating throughout the catalyst bed. This had been done previously by placing a two inch layer of porcelain chips on the bottom of the catalyst column. It was thought, however, that these might in some way affect the operation. Consequently the pipes supporting the catalyst were replaced in all the converters by a similar set, two inches longer.

The low boiling point products were caught in a

receiver surrounded by a jacket kept full of ice. Replenishing of the ice supply, however, required too much attention and time from the operator. To overcome this inconvenience a cooling water line was installed whereby cold water (18°C.) was kept flowing continuously over the catch pot.

Previous to these investigations the synthesis gas compressor was hand lubricated. This rather awkward means of lubrication was replaced by an automatic lubricator attached by means of a 3/16" steel drive shaft to the pulley of the compressor. The lubricator is the standard model ME manufactured by the Mills McCanna Company.

PROCEDURE

A. Catalysts and their Preparation

In the present investigations of Fischer-Tropsch catalysts at the University of Alberta five types of catalysts were prepared in the laboratory for testing while four catalysts were obtained from other sources. These were as follows:

1. U. S. Bureau of Mines No. 10 iron catalyst
2. U. S. Bureau of Mines No. 24 iron-copper catalyst
3. Iron-titanium catalyst
4. Cobalt-thoria-kieselguhr catalyst- U. S. Bureau of Mines, F.T.C. No. 12

Note: The above four catalysts have been prepared at the University of Alberta (12)

5. Cobalt-manganese catalyst
6. Co-ThO_2-MgO-kieselguhr catalyst - U. S. Bureau of Mines No. 89H
7. Cobalt-thoria catalyst (commercial) prepared by Harshaw Chemical Company, Cleveland, Ohio
8. Nickel-manganese catalyst (commercial) prepared by Harshaw Chemical Company, Cleveland, Ohio.

The water to be used in the catalyst preparations was tested for sulphur content, since, if present, it may be adsorbed on the surface of the catalyst and behave as a poison to the synthesis reaction.

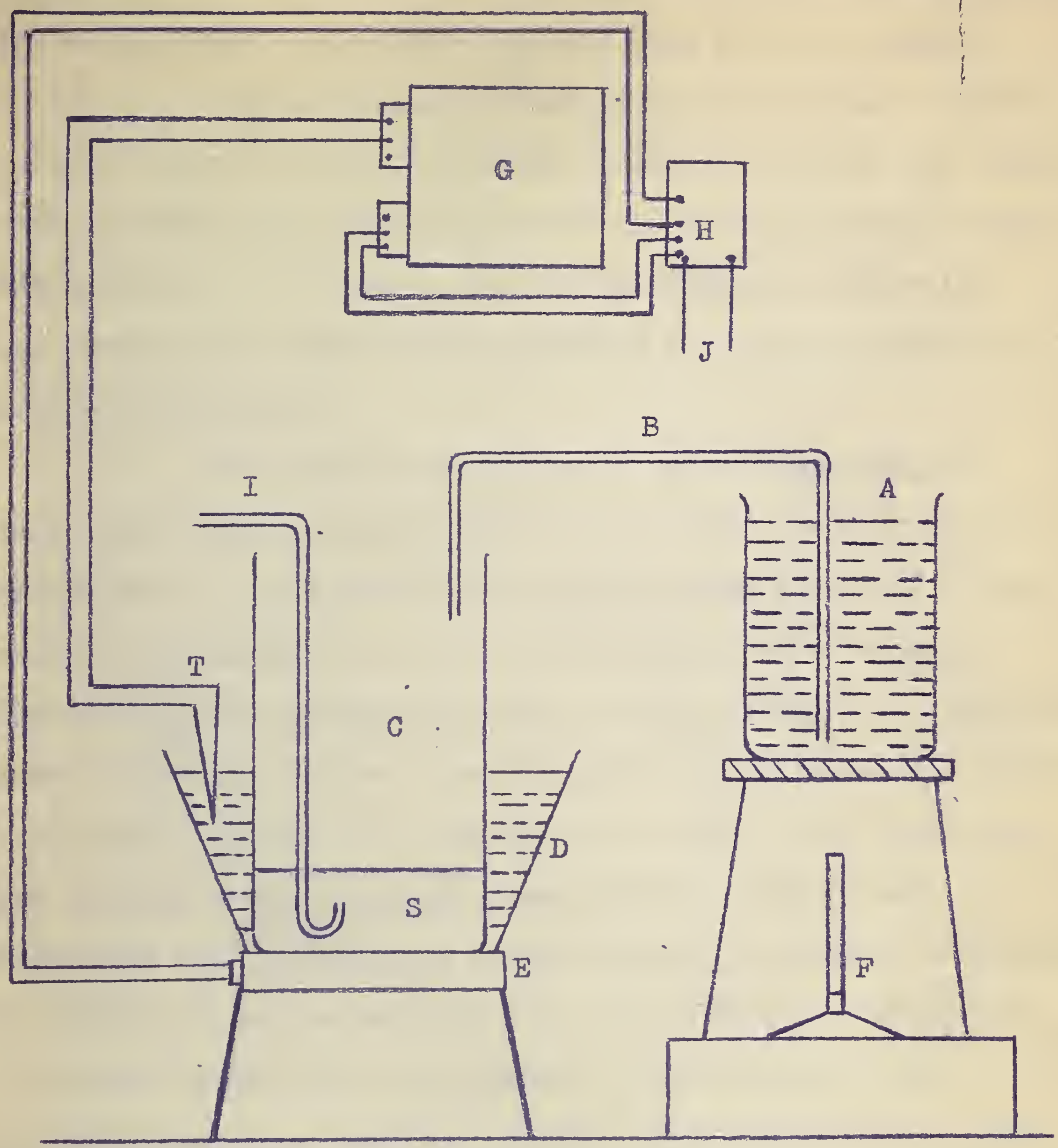
Very sensitive tests were made for hydrogen sulphide (40), total sulphides (1), sulphur dioxide (21)

and sulphites (20). Negative results were obtained for all these tests and hence it was assumed that if sulphur were present, it was in an amount too small to affect the catalyst in a harmful manner.

The procedure laid down by the U. S. Bureau of Mines was followed as closely as possible in the preparation of their catalysts. The equipment used is shown in Figure 9.

Bureau of Mines #10 Catalyst

Two solutions were made up to prepare this catalyst. The first was a solution 1012 gms. of $Fe(NO_3)_3 \cdot 9H_2O$ in three litres of distilled water and the second solution of 682 gms. of $K_2CO_3 \cdot 1\text{-}1/2\ H_2O$ in 890 ccs. of water. Both solutions were brought to a temperature of 70°C. and then the carbonate was slowly added to the nitrate by means of a dropping funnel. During the addition, which required twenty minutes, the slurry was vigorously stirred by a motor driven stirrer. Also during the addition the temperature varied between 68°-75°C. Heat at this time was supplied by a hot plate directly in contact with the slurry container, but close temperature control could not be maintained in this manner and hence the container was placed in a water bath. The slurry was made up to six litres, stirred and allowed to settle. The supernatant liquid was then decanted by means of a siphon. The slurry was again made up to six litres, stirred for five minutes, allowed to settle and decanted. Decantations were carried out to reduce the nitrate concentration to at least one part in sixteen thousand as determined by a diphenylamine test. Diphenylamine turns a



A - Hot water
B - Siphon
C - 15 litre slurry container
D - Water bath
E - hot plate
F - Bunsen burner
G - Micromax temperature controller
H - Electrostatic relay
I - Decanting siphon
J - 110 volt supply
T - Thermocouple

FIGURE 9 - APPARATUS FOR PREPARATION OF CATALYSTS

deep blue in the presence of nitrate. Twenty-one decantations were made before a negative nitrate test was obtained.

The decantations were carried out over a period of forty hours. Although it was attempted to keep the temperature at 70°C. it varied from 69°C. to 85°C. throughout the decantations. A micromax temperature recorder and relay were installed in the heating circuit for the preparation of the other catalysts.

The slurry was filtered in a large Buckner funnel and washed several times with water. It was then spread out on two unglazed porcelain plates in about a one-quarter inch layer and allowed to dry five days at room temperature. The dried material was then placed in a temperature controlled electric oven and the temperature was raised slowly over a period of five hours to 150°C. The oven was held at this temperature for twenty-four hours. Some difficulty was encountered in maintaining the oven temperature at 150°C., hence two auxiliary heating coils in series with a variable resistance were placed in the oven for the preparation of the other catalysts. A yield of 194 gms. was obtained.

The dried catalyst was ground to pass through a fifty mesh screen and to this powder nine grams of flaked graphite were added. The graphite is inert and has no catalytic action. The powder was then fed to a pelleting machine and pellets about 3/16" in diameter and1/8" thick were formed. The pellets so formed were quite hard and firm.

U. S. Bureau of Mines #24 Iron-Copper Catalyst

The reagents used were 700 grams of $FeSO_4.7H_2O$ and 133 grams $CuSO_4.5H_2O$ in three litres of water. These were coprecipitated from 692 grams of $K_2CO_3.1\text{-}1/2H_2O$ in 889 ccs. of water. The ratio of iron to copper in the resulting catalyst was four to one.

The temperature control, addition of K_2CO_3, washing and decantation were carried out in the same manner as for the iron catalyst, the only difference being that after each decantation the slurry was made up to six litres and air was blown through for ten minutes. This has the effect of oxidizing some of the iron to the ferric state. Decantations were carried out until a negative test for sulphate, as indicated by a $BaCl_2$ test, was obtained. After the eleventh decantation a large proportion of the solids would not settle out but remained in suspension in the colloidal state. Consequently, another one hundred grams of K_2CO_3 were added to precipitate this material. A negative test for sulphate was obtained after a total of twenty decantations. As with the iron catalyst the material after filtration was dried, baked, ground, mixed with ten grams of graphite and pelleted. The pellets obtained were quite hard and firm and the same size as the iron catalyst pellets.

Iron Titanium Catalyst

700 grams of $FeSO_4.9H_2O$ and 22.7 gms. of a 20% solution of $TiCl_3$ were coprecipitated from 700 grams of $K_2CO_3.1\text{-}1/2\ H_2O$. The techniques employed were the same as those used in the preparation of the U. S. Bureau of Mines

No. 10 iron catalyst. Seventeen decantations were carried out before a negative sulphate test was obtained. Flaked graphite to the extent of four percent was added to the dry powder before pelleting. The yield of catalyst was 225.5 grams.

Bureau of Mines F.T.C. #12 Cobalt Catalyst

The procedure used was that laid down by the U. S. Bureau of Mines except that the quantities used were one- and one-half times the specified amount:

$Co(NO_3)_2.6H_2O$	286 grams
$Th(NO_3)_4.12H_2O$	42.7 grams
$K_2CO_3.1\text{-}1/2H_2O$	280 grams
Celite H.C.S.-Johns Manville	90 grams.

The composition of the resulting catalyst is 82% cobalt oxide and 18% thorium oxide.

The cobalt and thorium salts were dissolved in two litres of distilled water at 86°c. The $K_2CO_3.1\text{-}1/2H_2O$ was dissolved in 300 ccs. of distilled water at about 90°C. These two solutions were brought to a temperature of 74°C. and then rapidly mixed. The resulting solution was diluted to six litres and agitated. Decantations were carried out as on the #10 iron catalyst until a negative nitrate test was obtained. Sixteen decantations were necessary. The slurry was then filtered.

The catalyst was then dried for thirty-four hours at room temperature and then for 20.5 hours at a temperature of 150 - 200°C. The dried material weighed 176.2 gms. This material was ground to pass through a fifty mesh

screen and eight grams of flaked graphite were then added. The powder was pelleted into very thin pellets since the material because of its lightness will not form firm pellets in one operation. The thin pellets were ground to pass a 40 mesh screen and the powder was repelleted. The pellets obtained were quite porous and low in mechanical strength.

The Bureau of Mines specified that the catalyst be dried for 24 hours at room temperature and for 20.5 hours at 151°C. However, this catalyst was dried at room temperature for thirty-four hours and the oven temperature reached 200°C. Hence another catalyst was prepared with better temperature control. The yield of this second catalyst was 195 grams. The procedure used for preparing this catalyst previously (66a) at the University of Alberta was identical except that the preparation was carried out over a longer period of time and conditions were more varied. The three catalysts were kept with the object in mind of comparing their activities in the synthesis.

Cobalt-Manganese Catalyst

The following materials were used for preparing the cobalt-manganese catalyst:

$Co(NO_3)_2.6H_2O$	237 grams
$Mn(NO_3)_2$ (80% solution)	63 grams
Celite H.C.S.-Johns Mansville	90 grams
$K_2CO_3.1\text{-}1/2\ H_2O$	227 grams

The procedure used in the coprecipitation of these materials was identical with that used in the preparation of the cobalt-thoria catalyst. An additional one hundred grams

of carbonate was added after the second decantation and a small amount after the eighteenth decantation to precipitate the solids which remained in suspension. In all, twenty-seven decantations were carried out before a negative nitrate test was obtained. Drying and pelleting were carried out as for the other cobalt catalyst. The yield was 174.6 grams.

Bureau of Mines Cobalt Catalyst No. 89H

This catalyst which was obtained from the U. S. Bureau of Mines had the following composition: Co:ThO_2:MgO:kieselguhr = 100:6:12:200 parts by weight. The catalyst was in the form of very small cylindrical pellets (1/8" diameter, 3/32" thick).

Commercial Cobalt and Nickel Catalysts

These were obtained from the Harshaw Chemical Company. Nothing is know of the composition of these two commercial catalysts. Cobalt and nickel are the bases and they are promoted by thoria and manganese respectively. Both catalysts were in the form of cylindrical pellets, 3/32" in diameter and 1/8" long.

B. Preparation of the Synthesis Gas for Catalyst Testing

The laboratory method for the preparation of synthesis gas by a batch operation is standard and has already been outlined in a previous report (12). However, the existing method of supplying methane from a high pressure cylinder to the tank A (Figure 3) required too much manual control and was discarded. Instead methane was drawn directly from the low pressure supply lines into a surge tank, which reduced pressure fluctuations, and thence

directly to the gas holder. Small pressure fluctuations between narrow limits could not be entirely eliminated. Quite accurate mixtures of gas were made in this way.

The additional synthesis gas purification equipment has been mentioned. The copper-zinc oxide purifier eliminated any oxygen, hydrogen sulphide or mercaptans which were still present in the gas, viz:

$$2Cu + O_2 = 2CuO$$

$$H_2S + ZnO = ZnS + H_2O$$

$$RSH + ZnO = ZnS + ROH$$

The water and ROH are subsequently removed in the alumina dryer.

An excess of water production in the preparation of synthesis gas over the nickel catalyst in the furnace indicated that the furnace temperature was too high or that the activity of the catalyst was impaired. During these tests, the catalyst was changed three times.

C. Analytical Methods and Operational Techniques

At the outset of these investigations the technique outlined by the U. S. Bureau of Mines for their catalysts was followed as closely as possible (6). However, yields of hydrocarbons obtained were insufficient and a new technique of reducing and conditioning the catalyst was employed. From the results obtained by this alternate method it is evident that the manner of reduction and the temperatures at which conditioning is commenced is of prime importance in determining the suitability of any catalyst.

The catalyst chambers were filled with pellets and tested for leaks. Any leaks were located and repaired. The converters were then ready for catalyst testing.

The testing operations consisted of three distinct procedures:

1. Reduction and conditioning of the catalyst
2. Operation on the conditioned catalyst
3. Analyses and material balances.

A discussion of the complete procedure follows.

Reduction and Conditioning of the Catalyst

A detailed account of the technique employed by the U.S. Bureau of Mines for reduction and conditioning of the catalyst is outlined in a previous report (12, 6). After testing a cobalt catalyst which had been reduced and conditioned by this method the yields were found to be unsatisfactory. It was thought that a considerable amount of the catalyst remained unreduced, and hence the reduction procedure was altered in some respects.

The system was first flushed with purified hydrogen at a rate of flow corresponding to a space velocity of 20-25 per hour. (Space velocities are based on the volume of the empty catalyst chamber.) The temperature was brought to 380°C. over a period of 20 hours. The hydrogen flow was continued at this temperature for twenty four hours. At this point the flow of hydrogen was increased to a space velocity of 200-300/hr. and held at this rate for two hours. The iron and cobalt catalysts were both reduced in this manner.

After the reduction of the iron catalyst in the aforementioned manner, the conditioning procedure outlined by the U. S. Bureau of Mines was employed. The catalyst temperature was reduced to 220°C., synthesis gas at a space velocity of 150/hr. was admitted and the pressure was raised to 100 psi. Once a steady contraction of 13% was obtained the temperature was raised to 250°C. over a period of forty-eight hours, after which time the catalyst was considered to be conditioned.

After the reduction of the cobalt catalyst the hydrogen flow was reduced to a small flow and the catalyst was cooled by reducing the pressure of the methane above the dowtherm to atmospheric pressure. Tetralin was then substituted for the dowtherm (b.pt. at N.T.P. = 205°C.). This fluid enabled the catalyst to be kept at initial conditioning temperature with a relatively low pressure (17" of Hg. vac.) above it. The temperature was lowered to 145°C.- 150°C. and a flow of synthesis gas at one atmosphere and a space velocity of 100/hr. was substituted for the hydrogen flow. This low initial temperature was employed to assure that sintering of the catalyst did not occur. The flow of synthesis gas at atmospheric pressure was registered on a calibrated water manometer since the existing manometer on the converter could not accommodate this ~~low~~ high flow. After a few hours the temperature was raised until a contraction of 20% was obtained. (This contraction was often obtained without raising the temperature.) This was held steady over a period of four hours. The temperature was again raised to give a contraction

of 30% and this was also held for four hours. This procedure was repeated until a 60% contraction was reached. This part of the conditioning generally required from one to two days. The water manometers were disconnected and replaced by the mercury manomoters and the pressure was raised to 100 psi. over a period of two hours. Production usually started with a contraction of 75 - 85%. The most active cobalt catalysts operate at a temperature of 190°C.

Method of Operation

On Sunday midnight of each week operation on the converter units commenced and was maintained until the following Saturday morning. The units operated continuously throughout this time unless repair necessitated shuting down for a short time. During such shut downs, passage of synthesis gas over the catalyst was discontinued and was replaced by a slight positive flow of purified hydrogen at atmospheric pressure. If the units were operating at 100 psi. the pressure was lowered to atmospheric over a period of an hour, and when synthesis gas operation commenced it was raised over the same period of time. After the units had been shut down the liquid products from the catch pots were removed.

Iron catalysts were tested at a synthesis gas space velocity of about 150/hour while cobalt catalysts were operated at a space velocity of 100/hour. At the end of a week's operation a notable decrease in the activity of the cobalt catalysts (as determined by the decreased contractions) occurred. Hence, after every shut down a low temper-

ature activation on the catalyst was performed. After the units had been shut down and the products drained, the catalyst temperature was raised to 15° above operating temperature, and a flow of hydrogen at a space velocity of 200-300 per hour was maintained for two hours. Iron catalysts are never reactivated since they maintain their activity for a period of several months. After this activation of the cobalt catalyst the flow of hydrogen was decreased to its former amount and the temperature was brought down to 10-15°C. below operating temperature. The units were left under these conditions until normal operation was recommenced.

Three operators maintained the operation of five units in three eight hour shifts. Each operator was responsible for some analysis work, maintenance and repairs on the units, preparation of synthesis gas and periodic recording of the operating conditions. Flow meters and manometers were read hourly, whereas temperatures and pressures were read every two or three hours. By means of this data, contractions were calculated and a close check on experimental conditions was maintained. A sample operating sheet is shown (page 118).

Exp't No. - 1
Catalyst - Fe
Weight - 1021

OPERATING SHEET
F - T

Date: Feb. 27/46

Reactor No. - 3
Nominal Pressure - 100
Nominal Temperature - 250°
Nominal Flow Rate - 150

Time	8 AM	9	10	11	12	1 PM	2	3	4	5	6	7	8	9	10	11	12	1 AM	2	3	4	5	6	7
PRESSURES																								
Reactor psi. gauge	99		100		100		100		100		100		100		100		100		100		99		99	
Jacket	2#		2		2		2		2		2		2		2		2		2		2		2	
Barometer mm. Hg	685		685		685		685		685		685		685		683		683		683		684		684	
TEMPERATURES																								
Catalyst 1	248		248		247		247		247		248		247		248		248		251		251		251	
Catalyst 2	252		252		252		253		253		252		253		252		252		254		254		254	
Catalyst 3	243		243		243		244		244		243		244		243		243		247		247		247	
Jacket °C	253		253		252		253		253		253		253		253		253		254		254		254	
Gasmeter °C	78		78		78		78		78		78		79		79		77		77		77		77	
FLOW																								
Gasmeter-cu.ft.	68.0120	68.2320	68.4910	68.7550	69.0200	69.2540		69.7600	70.2940		70.8120	71.3210	71.5730	71.7950		72.2250	72.4070	72.5690	72.7542	72.9390	73.1233	73.3076	73.4919	73.6762
Flowmeter L	1.90	1.80	2.00	1.90	1.90	1.80	1.80	1.80	1.80	1.70	1.80	1.80	1.95	1.95	2.00	1.80	1.90	2.00	2.00	1.90	1.90	2.00	1.90	2.00
" R	2.00	1.90	2.05	1.95	1.95	1.90	1.90	1.90	1.90	1.80	1.90	1.85	2.00	2.00	2.05	1.85	1.95	2.00	2.00	1.95	2.00	2.00	1.95	2.00
" Total	3.90	3.70	4.05	3.85	3.85	3.70	3.70	3.70	3.70	3.50	3.70	3.65	3.95	3.95	4.05	3.65	3.85	4.00	4.00	3.85	3.90	4.00	3.85	4.00
% Decrease		30.8			31.5			30.0		30.3			38.2			55.3		54.3			51.6		51.5	
Samples			3C23								3C24								3C25					

Notes:

Notes:

Notes:

Analyses and Material Balances

The synthesis gas was analyzed at least once a week in a standard Burrell Gas Analysis Apparatus to keep a check on the $CO:H_2$ ratio. During these investigations the average ratio of $H_2:CO$ in the synthesis gas was 2.09:1.

The residue gas was collected in a two litre proportional sampler over a period of several hours. One gas analysis was performed on each shift. The residue gas contained water vapor, CO_2, hydrocarbons (CH_4, C_2H_6, C_3H_8), N_2 and unconverted CO and H_2.

The water vapor was removed by a $CaCl_2$ U-tube drier and was determined by weighing before and after a week's operation. The CO_2 was removed by a caustic scrubber containing 250 ccs. of approximately 3N.KOH. The CO_2 content was determined by titrating a 10 cc. aliquot part of the spent solution against standardized 1.5 N.HCl using phenolpthalein and methyl orange indicators. For iron catalysts these titrations were carried out every 8 hours since much CO_2 was produced but for cobalt catalysts titrations were carried out after a week's operation.

The CO_2 and water free residue gas was analyzed in the Burrel Gas Analysis Apparatus to determine the percentages of CO_2, CO, H_2, CH_4, C_2H_6 and N_2.

The liquid product that was collected at the end of each run was allowed to accumulate until a sufficient amount of the sample had been obtained for analyses. Some water condensed with the hydrocarbon product and this was also analyzed. Solids were removed from the product by

filtration. The following tests were carried out on the liquid hydrocarbon products (65a):

(a) Density - density bottles calibrated with water at 25°C. were used.

(b) Refractive index - an Abbé refractomer was used.

(c) A.S.T.M. aniline point - only a small amount of sample was available, therefore 1 cc. of aniline and 1 cc. of sample was used instead of 10 ccs. of each as specified. An aniline point indicates the temperature at which equal volumes of aniline and sample become completely miscible. The more unsaturated the oil, the lower the resulting aniline point. A.S.T.M. (D-611-44T)

(d) A.S.T.M. (D94-36) saponification number - a measured quantity of the acid free sample was heated and refluxed with a measured amount of alcoholic potassium hydroxide. The number of milligrams of KOH adsorbed by 1 gram of oil, as determined by a back titration with standard HCl, is known as the saponification equivalent. The test is a measure of the free and combined fatty acid in the sample.

(e) A.S.T.M. distillation (D86-35) - because of the small amounts of sample available a 10 ml. distillation flask was used instead of a 100 ml. flask. The distillation was arbitrarily stopped at 250°C. to prevent waxes and high boiling point oils from solidifying in the condenser. The data was used to plot distillation curves.

Only the approximate density was determined for the high boiling fraction. This was done by weighing the

volume of wax drained from the pots at the end of each run.

The water that condensed with the oil fraction was subjected to the following tests:

(a) Density

(b) A distillation to detect the presence of low boiling organic compounds. A 250 cc. distilling flask fitted with an Illinois type column packed with a nichrome spring was used.

(c) A qualitative test for alcohols - a few drops of ceric nitrate was mixed with a small amount of sample and the presence of alcohols was indicated by a change of color from yellow to red. This test can be used for alcohols with less than ten carbon atoms. Aldehydes, ketones and esters do not interfere (66B).

(d) A qualitative test for aldehydes and ketones - a small portion of the sample was treated with 3 cc. of 2,4 dinitrophenyl hydrazine reagent, a positive test being indicated by the formation of a precipitate (66B).

A material balance was carried out on the Co-ThO_2 catalyst number three. A sample calculation is shown in Appendix A.

EXPERIMENTAL RESULTS AND DISCUSSION

During the present investigations ten catalysts were tested:

Iron-copper #1
Iron-copper #2
Pure iron #3
Cobalt-thoria-kieselguhr #1
Cobalt-thoria-kieselguhr #2
Cobalt-thoria-kieselguhr #3
Cobalt-thoria (Harshaw)
Cobalt-thoria-magnesia-kieselguhr (U.S.Bureau of Mines)
Cobalt-manganese-kieselguhr
Nickel-manganese (Harshaw)

Each catalyst was given a separate series of tests. The treatment of each catalyst and the results thereby obtained are summarized in tabular form, the figures presented being an average for each run. A discussion of each catalyst follows the tabulated results.

The synthesis gas used throughout these tests contained over 95% carbon monoxide and hydrogen with an average H_2:CO ratio of 2.08:1. A sensitive test (40) which would detect hydrogen sulphide in concentrations of 0.1 parts per million was carried out on a sample of this gas and a negative result was obtained.

The main objective in the catalyst testing was to obtain high yields of liquid hydrocarbons, secondary emphasis being placed on the type of product obtained. Long term tests to determine the ultimate life of any catalyst

were not carried out. A catalyst was discarded after continued testing indicated that yields obtained were unsatisfactory.

Iron-Copper Catalyst No. 1

Source - prepared at the University of Alberta
by A. C. Shaw (66a)

Weight used - 74.5 gram.

This catalyst was the first to be tested by the authors, and was used by them primarily to become more familiar with operating procedure, and with the logical collection of necessary data. Hence, the information obtained on the performance of this catalyst is not as complete as that obtained in subsequent tests on other catalysts.

The following tables briefly summarize the history, yields and other pertinent data regarding this catalyst.

Table 8

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Starting Cont. %
1	57	Short reduction	368			
		Conditioning	209-232	0-16		
2	99	Operation	234-250	16-48	231	16
3	96	Operation	244-256	31-53	246	31

Table 9

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.33	66.55	29.70	---------3.92--------		
2	0.00	6[illegible].00	18.40	---------13.00--------		
3	0.00	70.30	14.40	---------15.34--------		

No data was obtained on the individual hydrocarbon contents of the residual gases from this catalyst. However, the average nitrogen content can be assumed to be approximately 3% by volume, so that an estimate of the total gaseous hydrocarbons present can be made from the above table.

Table 10

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m.					% Conversion to Cond. Hyd.
	Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	
1	0.0	4.08	4.08	X	20.1	1.9
2	6.11	5.77	11.88	83.6	23.0	5.7
3	7.39	7.77	15.16	106.0	26.2	7.2

X No data

Discussion

In these data tables and the subsequent tabulations for the other catalysts tested, the results obtained are summarized for each experimental run made. A run was was considered completed every time the unit was shut down and liquid hydrocarbons were drawn off. The number of hours of the run then refers only to the actual length of time synthesis gas was passed over the catalyst during this period.

The terms describing the chronological treatment

of the catalysts in Table 8, refer to the standard procedures which have been outlined in a previous section. The temperature, or temperature range, and the contraction range given, show the minimum and maximum figures for that run. In general, during the course of the test, the data varied in a fairly regular manner between these two limits.

When starting operation after a regular shutdown it was customary to commence with the operating temperature below the normal when the synthesis gas was initially entered. This procedure was adopted to prevent an excessive rise in temperature due to the initial liberation of heat of reaction. The catalyst temperature was then brought to normal operating level. The starting temperatures and the corresponding contractions are also given in Table 8.

Tables 9 and 10 show respectively the average analyses of the residue gas and the observed hydrocarbon yields for each run. The majority of the carbon dioxide produced was removed in caustic scrubbers prior to gas sampling, and therefore only small amounts appear in the gas analyses. The percent conversion to solid and liquid hydrocarbons is based on the theoretical yield of 200 grams per cubic meter for a synthesis gas having a H_2:CO ratio of 2:1.

Although relatively high contractions were obtained with this catalyst during most of the 282 hours of operation, yields were unsatisfactory. The synthesis gas used had a hydrogen to carbon monoxide ratio of 2:1 rather than the optimum 1:1 ratio required for this type of catalyst. The over abundance of hydrogen probably serves only as a diluent. Hence a 80% contraction using 2:1 synthesis gas indicates a satisfactory rate of reaction.

It will be noted that the amount of gaseous hydrocarbons formed increased considerably as the operating temperatures were raised, as did the amount of light liquid hydrocarbons formed.

It appears that somewhat larger amounts of carbon dioxide were produced than the yields warrant. It is possible that the water gas shift might have occurred to some extent, which would consume carbon monoxide and give excessive amounts of hydrogen and carbon dioxide. This supposition is supported by the data in Tables 9 and 10.

Although this catalyst was given only a short reduction at low space velocities, it appears to be as active as other iron catalysts which were more fully reduced. According to latest reports (8), no special significance is attached to the formation of a certain amount of water during the Fischer-Tropsch synthesis using iron catalysts.

In conclusion, it would appear that this preparation was the most active iron catalyst tested. Given more strenuous reduction, and more careful operating control, greatly improved performance might be expected.

Iron-Copper Catalyst #2

Source - prepared by the authors using the
Bureau of Mines procedure

Weight used - 33.6 grams.

Since the yields obtained with another iron-copper catalyst (12) were not high, it was decided to prepare and test another catalyst of the same composition. It was

thought that perhaps more care in the preparation might produce a catalyst giving more satisfactory yields.

Tables #11, 12 and 13 are a summary of the data obtained.

Table 11

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Starting Cont.%
1	117	Long reduction	370			
		Conditioning	219-240	13-31		
		Operation	240-253	31-41		
2	123	Operation	230-255	28-31-47	232	
3	92	Operation	230-254	40-52	237	40
4	122	Operation	238-255	38-47	247	
5	122	Operation	250-272	41-52	243	

Table 12

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.00	64.90	16.43	11.29	3.74	3.63
2	0.14	71.35	11.14	9.90	2.91	4.50
3	0.38	72.30	14.05	4.27	4.20	3.88
4	0.00	78.20	10.52	4.38	3.06	3.22
5	0.00	74.20	7.97	3.46	9.32	5.10

Table 13

Yields - Gms/cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m. Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	% Conversion to Cond. Hyd.
1	4.06	7.19	11.25	133.6	20.3	5.4
2	11.30	6.35	17.65	165.0	31.4	8.5
3	16.86	6.05	22.91	169.3	25.2	11.0
4	8.21	2.30	10.51	181.0	—	5.0
5	9.10	2.60	11.70	194.0	33.7	5.6

Discussion

Initially a long reduction was given to this catalyst. No subsequent reductions were used during the 376 hours of synthesis gas flow.

Figure 10 shows the plot of hours of synthesis gas flow versus percent contraction for runs #1 and #2. The curves are of the same general shape, differing in the degree of the contraction. It was noticed that the curves for run numbers 3, 4 and 5 if plotted would have closely paralleled run #2 except for the early hours of synthesis gas flow. A relatively high contraction has been maintained throughout without producing high yields of solid or liquid hydrocarbons.

The possibility of the water gas shift reaction having taken place to produce the high yields of carbon dioxide and hydrogen can not be discarded.

Towards the end of the run #1 it was decided to operate at a temperature of 263°C, to attempt to increase the activity of the catalyst. This increase of 5° above the normal operating temperature did not produce the desired result in any of the four runs where it was employed. It

[illegible]

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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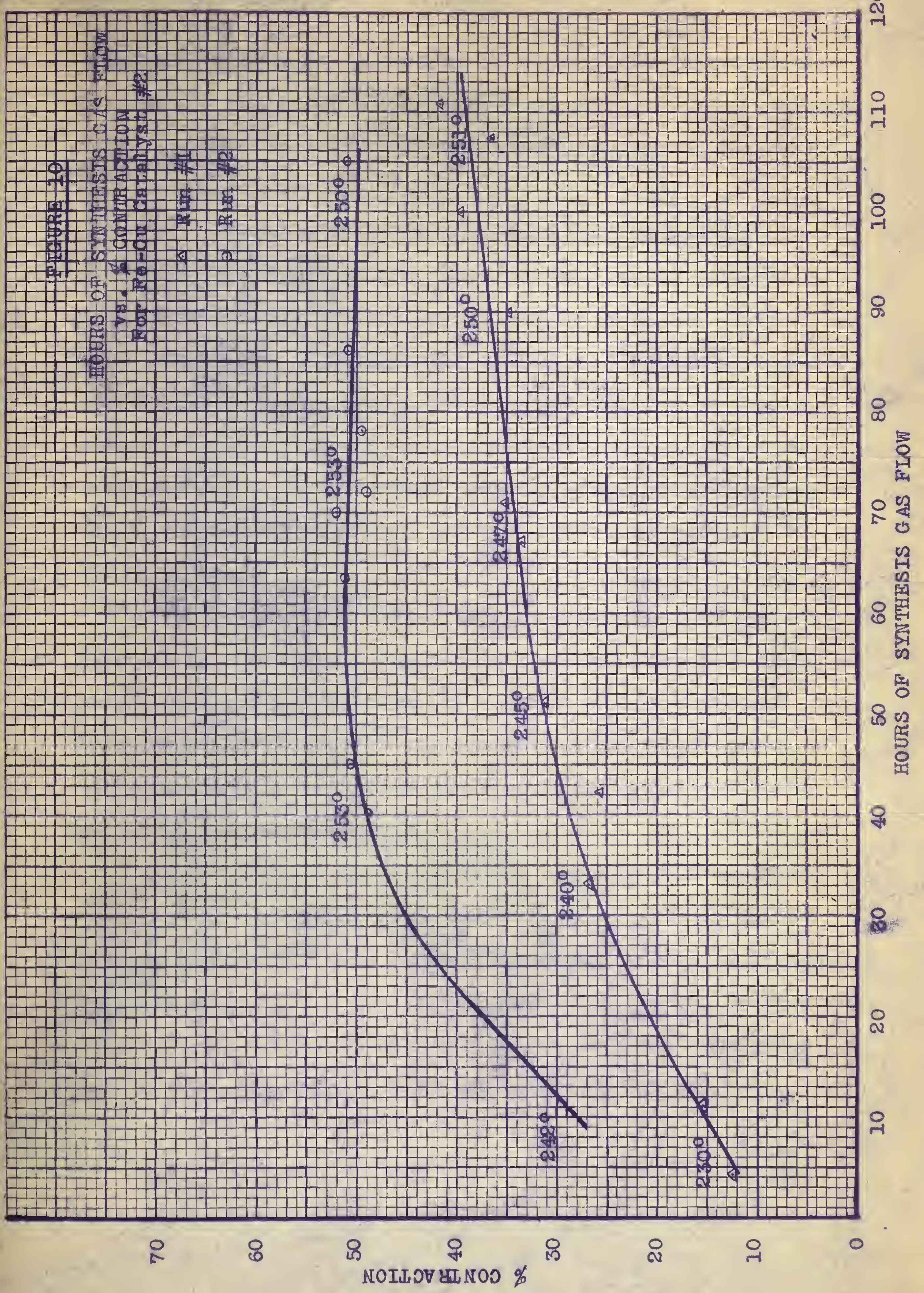

FIGURE 10

HOURS OF SYNTHESIS GAS FLOW
vs. % CONTRACTION
For Fe-Cu Catalyst #2

was then decided to operate at a still higher temperature. At the end of run #5 a temperature of 272° was being employed, which is 22° above the recommended operating temperature for this catalyst (6).

The effects of increased temperature are clearly shown in tables 12 and 13. The yields of solid and liquid hydrocarbons remained small while yields of carbon dioxide were excessive. The average analyses of the residue gas for the runs show a hydrogen content above the average with a relatively small carbon monoxide fraction. This is especially true for run #5. The ethane production has been increased about three fold with this 22° increase in operating temperature.

The fact that a $2H_2:1CO$ synthesis gas was used instead of the $1H_2:1CO$ gas recommended for such catalysts, would account only in part for the low yields obtained. The average yield of product for the 5 runs was 14.20 grams per cubic meter with a maximum yield of 22.01 grams per cubic meter of synthesis gas.

Again the catalyst has not attained expected yields (6). Reactions have occurred which produce mainly carbon dioxide and some gaseous hydrocarbons with only small amounts of solid and liquid hydrocarbons. It may be that the very excessive amounts of hydrogen in a $2H_2:1CO$ synthesis gas is more detrimental than was at first thought.

Iron Catalyst #3

Source - prepared at the University of Alberta
by the authors

Weight used - 108.1 grams.

The summary of the results obtained from the operation of this iron catalyst is given in tables 14, 15 and 16.

Table 14

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Conv. Range %	Starting Temp.	Starting Conv. %
1	65	Short reduction	374			
		Conditioning	219-250	1.5-17		
		Operation	240-290	3-8		
2	116	Long reduction	377			
		Conditioning	230-350	30-46		
		Operation	243-254	32-57		
3	123	Operation	251-255	19-55	214	6-19
4	113.5	Operation	251-266	25-55	206	

Table 15

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
2	0.10	62.80	18.90	14.10	4.00	0.10
3	0.43	60.66	28.21	6.23	0.39	4.07
4	0.18	67.80	15.52	7.08	5.80	3.62

Table 16

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m. Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	% Conversion to Cond. Hyd.
1	trace		trace	24.00	63.40[x]	
2	3.00	1.64	4.64	40.00	22.90	2.2
3	1.47	1.24	2.71	53.80	21.55	1.3
4	2.90	1.23	4.13	147.20	51.80	2.9

---

[x] This excess amount of water partly arises from the reduction of the oxide catalyst.

Discussion

It can be noted in run #1 (table 14) that conditioning was completed at a temperature of 230°C. and that the operating temperature varies between 240° and 250°C. The short reduction resulted in very low contractions and hence at the start of run #2 the catalyst was given a long reduction. This procedure resulted in increased contractions throughout the remaining operating periods. The catalyst was operated for a total of 417 hours.

In all runs but #1 carbon dioxide was the main oxygenated product; however considerable amounts of water were also produced. The fact that a synthesis gas of composition H_2:CO = 2:1 was used for testing this catalyst, whereas a synthesis gas containing a ratio of H_2:CO = 1:1 is the optimum for such a catalyst, probably had a bearing on the small yields of liquid hydrocarbons obtained.

Since this synthesis gas had a high hydrogen content it would possibly promote a reaction such as :

$$CO + 3H_2 = CH_4 + H_2O$$

This supposition is borne out somewhat from the data in table 16 for run #1 where it is observed that only a trace of liquid hydrocarbons was produced, whereas the gas analysis showed a methane content of 14.1 percent. The predominant production of water with this catalyst is also significant from a consideration of the above equation.

On the whole behavior of this catalyst was not uniform and the yields obtained were much too low. Different and more satisfactory results probably could be obtained if a synthesis gas of hydrogen to carbon monoxide ratio of 1:1 were used.

Cobalt-Thoria-Kieselguhr Catalyst #1

Source - prepared at the University of Alberta
by the authors

Weight used - 32.8 grams.

This catalyst was the second cobalt-thoria catalyst prepared by the authors. This preparation was accurately controlled in the precipitation and drying steps.

The treatment, yields and other data concerning this catalyst are presented in the following tables.

Table 17

History of Catalyst

Run No.	Fre.Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Starting Cont.%
1	120	Short reduction	376			
		Conditioning	147-196	25-44		
		Operation	195-197	41-37		
2	112.5	Operation	193-198	48-63		
		Low temp.act.	210			
		Operation	193-190	91-50	197	91
3	72	Long reduction	376			
		Conditioning	150-195	25-30		
		Operation	195-200	50-65		
4	108.5	Low temp. act.	200			
		Operation	192-200	72-42	192	72
5	90.5	Low temp. act.	210			
		Operation	195-200	79-50	199	68
6	25	Low temp. act.	212			
		Operation	190-201	66-57	195	68

Table 18

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.12	62.0	26.6	2.35	2.15	4.00
2	0.92	64.7	21.8	-----------12.02-----------		
3	0.17	56.9	26.7	-----------16.05-----------		
4	0.00	49.5	28.5	14.81	2.70	4.08
5	0.00	47.9	28.7	19.35	0.00	4.04
6	No data					

Table 19

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m. Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	% Conversion to Cond.Hyd.
1	2.32	9.00	11.32	10.07	55.2	5.4
2	1.55	21.60	23.15	7.32	74.2	11.1
3	6.25	37.00	43.05	6.39	115.0	21.0
4	7.73	46.50	54.23	9.56	123.5	26.0
5	6.89	33.10	39.99	10.49	120.2	19.8
6	10.02	53.00	63.02	26.28	164.5	30.1

Discussion

The most important result obtained during the tests on this catalyst can best be observed from the data given in Table 19. The catalyst was given the standard short reduction at a low space velocity, and after two weeks operation gave only small yields. A long reduction was then given the catalyst, using the procedure described earlier. A definite increase in yields was obtained in all subsequent runs without any change being made in the operating technique. Thus it would appear that the Bureau of Mines procedure does not reduce this particular catalyst sufficiently to insure maximum activity.

The time-contraction curves (Figure 11) show the behavior of this catalyst after the long reduction. The conditioning curve is typical of a fairly active catalyst. In the initial operating period contractions dropped off rapidly, but after an activation a more gradual decrease in contraction was obtained in run #4 and in subsequent runs.

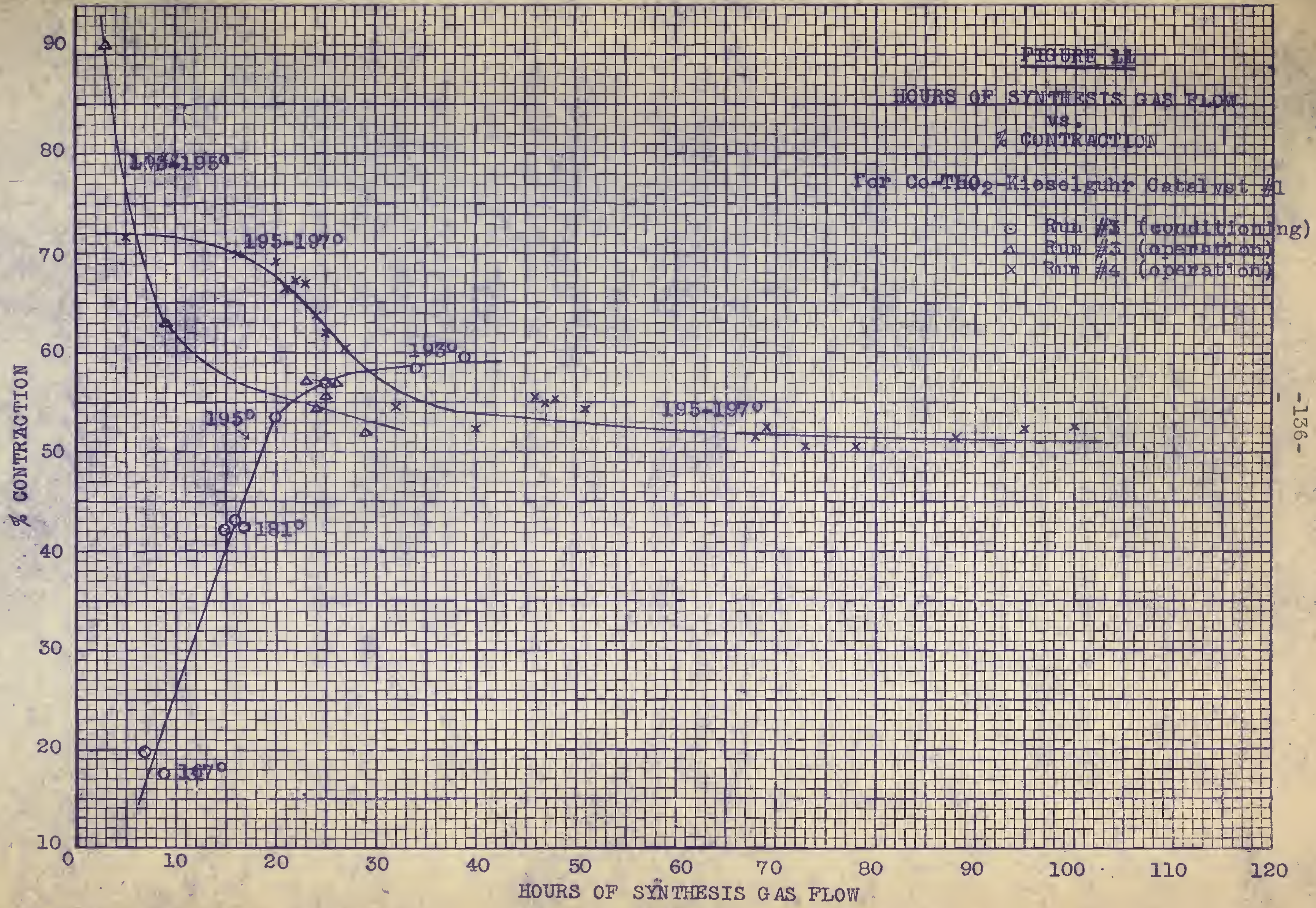

FIGURE 11

HOURS OF SYNTHESIS GAS FLOW
vs.
% CONTRACTION

For Co-ThO$_2$-Kieselguhr Catalyst #1

The long reduction did not result in any significant increase in the amounts of gaseous hydrocarbons formed. Hence, it is possible that the catalyst in a partially reduced form can serve to catalyze the formation of methane and ethane, while not possessing a sufficient number of active centers to permit the production of large amounts of higher hydrocarbons.

The maximum yield of 64.02 grams per cu.m. from this catalyst was obtained during a short run after an activation, when the rate of conversion was at a maximum.

The product obtained contained a large percentage of waxes and heavy oils. This was probably due to a slightly higher content of alkali in the catalyst than was desirable for the production of gasoline range hydrocarbons. During the preparation of this catalyst it was found necessary to maintain an excess of electrolyte and thus more of the alkali was present in the final product than was desirable. It was found by other workers (75) that excess alkali caused polymerization of the -CH_2- groups on the catalyst surface to proceed to a greater extent, thus producing larger amounts of heavy waxes. The formation of this heavy wax was very probably a contributing factor to the relatively rapid decline in catalyst activity.

In view of the small amount of catalyst used, and taking into account the excessive wax formation, this catalyst appeared to have a good activity. However, the yields obtained still fell considerably short of those obtained by other workers using similar catalysts. It is possible that

if a strenuous reduction had been used initially, a better performance might have resulted.

Cobalt-Thoria-Kieselguhr Catalyst #2

Source - prepared at the University of Alberta by
A. G. Shaw (66a) using Bureau of Mines
procedure.

Weight used - 40.2 grams.

This catalyst has been previously tested (12) and a second test was carried out to confirm or improve upon earlier yields.

Tables number 20, 21 and 22 summarize the data obtained in this second test.

Table 20

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Starting Cont. %
1	130	Short reduction	378			
		Conditioning	181-196	12-34		
		Operation	190-197	34-39		
2	113	Operation	198-200	38-32	185	55.5
		Low temp. act.	200			
		Operation	190-200	31-42	174	54.0
3	73.5	Long reduction	379			
		Conditioning	180-200	4-32		
4	104	Low tempera.act.	204			
		Operation	189-199	91-58	186	
5	97	Low temp. act.	207			
		Operation	193-199	83-50	181	
6	21	Low temp. act.	215			
		Operation	195-199	77-79	188	77.9

Table 21

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.07	65.11	29.40	1.68	1.70	2.00
2 1st op.	0.00	60.41	30.23	1.33	3.60	4.42
2nd op.	0.00	59.25	30.00	2.11	3.75	4.78
3	No data					
4	0.12	46.93	16.90	16.69	9.20	10.08
5	0.12	44.25	24.35	19.98	3.07	8.21
6	No data					

Table 22

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m.					% Conversion to Cond.Hyd.
	Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	
1	3.62	7.00	10.62	0.97	46.6	5.1
2	5.94	15.00	20.94	16.50	66.8	10.0
3	11.00	16.75	27.75	7.[illegible]	86.2	13.3
4	14.45	32.60	47.05	14.95	140.2	22.6
5	9.68	32.45	42.13	10.71	127.8	20.2
6	17.70	98.60	116.30	22.36	225.5	55.7

Discussion

During a total of 530 hours of synthesis gas flow this catalyst was given a short reduction, a long reduction and four low temperature activations.

The four hour reduction initially given to the catalyst resulted in low contractions for the conditioning

and the three operational periods which followed. Since the maximum yield was only 27.75 grams per cubic meter, it was decided that another reduction using a longer period of time was necessary to be certain that a larger portion of the oxide was removed from the catalyst.

The twenty-four hour reduction appears to confirm this latter point. The contractions during conditioning were raised considerably. In the three operational periods which followed, the contractions and yields were much improved over previous results. The yield of 116.30 grams per cubic meter of synthesis gas is explained by the shortness of the run, which followed a low temperature activation. The same may be said for the yields of carbon dioxide and water.

In Figure 12, time in hours of synthesis gas flow has been plotted against percent contraction for three runs. The curve for the conditioning is the type which would be expected - increasing contraction as the temperature is raised until an almost constant contraction is reached. Run #4 is the most successful of the two runs which followed the conditioning. A slower rate of decline of contraction is shown by the graph. This is probably due to the amount of revivification given by the low temperature activation - the necessary conditions to obtain the higher activity still remaining obscure.

Operating temperatures range from 180° to 200°C. This latter temperature corresponds to the maximum recommended by the Bureau of Mines when using this catalyst. Starting

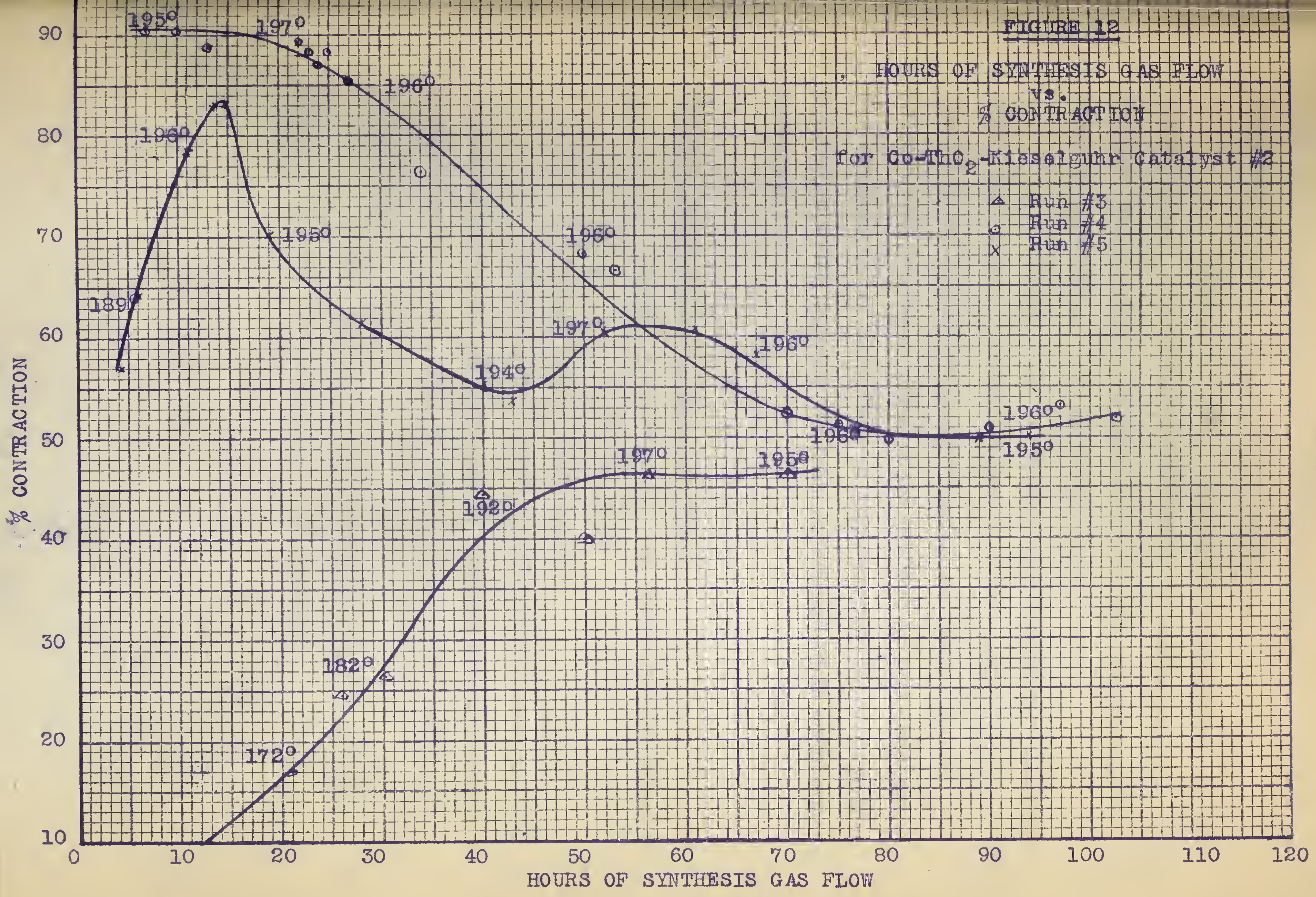

FIGURE 12

HOURS OF SYNTHESIS GAS FLOW
vs.
% CONTRACTION

for Co-ThO$_2$-Kieselguhr Catalyst #2

temperatures range from 174° to 198°C.

Table 21 shows the average composition of the residue gas. The hydrogen and carbon monoxide contents decline as the yields of solid, liquid and gaseous hydrocarbons increase. This is as expected.

While this catalyst has not shown the activity which the Bureau of Mines information (6) would indicate, the yields obtained and the high initial contractions are encouraging factors. More rigid control in the catalyst preparation, along with further improvements in operating technique, would warrant further experimentation with this catalyst.

Cobalt-Thoria-Kieselguhr Catalyst #3

Source - prepared at the University of Alberta
by the authors

Weight used - 41.9 grams.

This was the first cobalt-thoria catalyst made by the authors, and the preparation was not as accurately controlled as in the case of the cobalt-thoria-kieselguhr catalyst #1.

The following tabulations summarize the data obtained during the testing of this catalyst.

Table 23

History of Catalyst

Run No.	Hrs.Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Starting Cont.%
1	69.0	Long reduction	376			
		Conditioning	150-200	6-55		
2	24.5	Low temp. act.	210			
		Operation	195-198	95-47	183	
3	80.0	Low temp. act.	210			
		Operation	195-199	86-49	195	75
4	117.0	Low temp. act.	210			
		Operation	195-208	80-62[x]	176	50
5	117.0	Low temp. act.	215			
		Operation	196-206	67-40	190	
		Low temp. act.	215			
		Operation	196-206	72-45	180	80
6	86.0	Low temp.act.	215			
		Operation	195-200	71-51	190	46

[x] Gas leak in converter

Table 24

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.12	55.40	28.00	9.03	2.72	4.08
2	No data					
3	0.24	59.70	31.10	0.54	3.50	5.02
4	0.24	53.30	25.00	9.23	2.83	3.90
5	0.27	54.50	29.00	4.71	3.97	6.06
6	0.29	53.00	31.10	5.40	3.12	6.49

Table 23

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m.					% Conversion to Cond. Hyd.
	Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	
1	11.40	25.95	37.35	16.27	111.3	17.0
2	13.02	64.60	77.62	16.50	194.0	37.2
3	10.70	40.00	50.70	13.45	125.2	24.2
4	7.20	28.50	35.70	11.66	104.7	17.1
5	6.35	35.80	42.15	15.27	128.9	20.2
6	5.64	30.60	36.24	17.20	124.3	17.3

The low yield obtained for run #4 is in error, since two gas leaks were found in the converter during operation. Hence, a smaller amount of synthesis gas than that calculated had actually been passed over the catalyst. If calculations were based on this smaller amount it would have the effect of increasing the yields to a greater value per unit of synthesis gas.

Discussion

This catalyst was given an initial long reduction, and was conditioned in the normal manner. Synthesis gas was passed over the catalyst for a total of 493 hours and during this time six low temperature activations were carried out. This catalyst did not exhibit any marked activity. The maximum yield was obtained during a short run immediately following an activation when conversion was proceeding at a high rate. Contractions with this catalyst dropped off slightly more rapidly than was the case for the second catalyst of the same composition, which had been previously tested.

This can be seen clearly from the accompanying time-contraction curves (Figure 13). The contraction decline, for all three cases shown, indicates that this catalyst underwent a more rapid decrease in activity than the second identical preparation. This was to be expected since this catalyst had not been as carefully prepared.

It will be noted that the residual gas in most cases contained a greater proportion of carbon monoxide than the inlet gas, that is, the off-gas was hydrogen-poor. This would indicate a saturated hydrocarbon product, especially in the light and gaseous fractions.

In the last three runs, higher operating temperatures were used in an attempt to increase the catalyst activity. From the data it is apparent that no advantage was obtained by operating at temperatures above the optimum, that is, above 200°C. In fact, catalyst activity and therefore yields showed a decrease at the higher temperatures.

Cobalt-Thoria Catalyst (Harshaw)

Source - a commercial catalyst prepared by the Harshaw Chemical Company. The method of preparation is unknown to the authors.

Weight used - 62.1 grams.

This catalyst had been tested previously (12). Further testing was employed to confirm or improve the yields obtained at that time.

Tables 26, 27 and 28 are a summary of the data obtained from this catalyst.

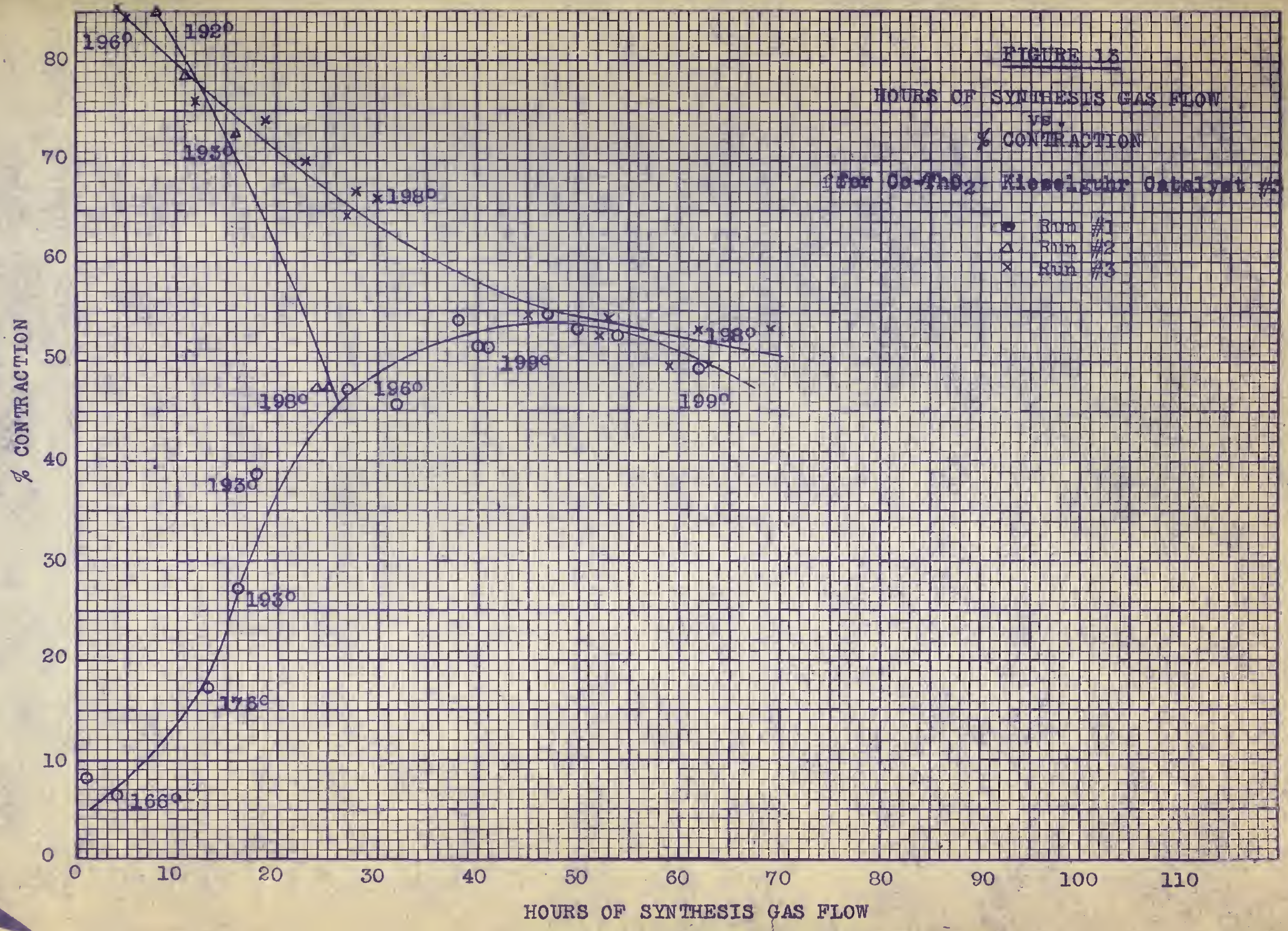

FIGURE 13

HOURS OF SYNTHESIS GAS FLOW
vs.
% CONTRACTION

for Co-ThO$_2$-Kieselguhr Catalyst #3

Table 26

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Conv. Range %	Starting Temp.	Starting Conv. %
1	70	Long reduction	376			
		Conditioning	150-197	10-56		
2	28	Low temp. act.	207			
		Operation	192-197	86-50	192	86
3	61	Low temp. act.	215			
		Operation	194-200	91-63	186	
4	123	Low temp. act.	215			
		Operation	185-202	85-47-64	172	69
5	119	Low temp. act.	215			
		Operation(72hrs.)	190-203	92-55	176	
		Low temp.act.	215			
		Operation(47hrs.)	192-200	91-50	189	91
6	85.5	Low temp. act.	214			
		Operation	196-201	78-49	181	78

Table 27

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.00	58.23	31.50	4.76	1.31	3.82
2	0.37	56.90	30.20	6.65	2.12	3.71
3	0.12	45.75	23.90	18.23	4.56	7.53
4	0.04	53.60	29.63	10.07	3.86	2.84
5	X0.00	50.10	20.00	18.01	2.75	8.15
	X0.14	49.18	26.30	10.05	2.66	11.71
6	0.06	52.90	30.40	9.28	2.76	4.70

X First and second operating periods

Table 22

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m. Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	% Conversion to Cond. Hyd.
1	5.45	16.38	21.83	11.40	60.0	10.4
2	15.05	71.60	86.65	19.56	213.0	41.5
3	9.40	35.60	45.00	13.30	132.5	21.6
4	9.13	34.50	43.63	12.22	124.8	20.9
5	9.06	38.40	47.46	13.32	130.9	22.7
6	7.50	32.50	40.00	14.53	157.1	19.2

Discussion

This catalyst was given an initial long reduction with no subsequent reductions. After the conditioning period a cycle of low temperature activations and operations was carried out, six activations being given during the total running time of 806 hours.

Figure 14 shows the effect of time and temperature on the contractions for run #1, 2 and 3. The curve for the conditioning period is very similar to other time contraction curves for cobalt catalysts. The constant temperature curve for run #2 shows a rapid drop in contraction with increasing time. In run #3 an attempt to compensate this drop by gradually increasing the temperature resulted in a more gradual decrease in contractions. It would appear that the average contraction after a period of days would be considerably lower in the case of run #2 than in the case of run #3. In other cases, contrary to this tendency, the

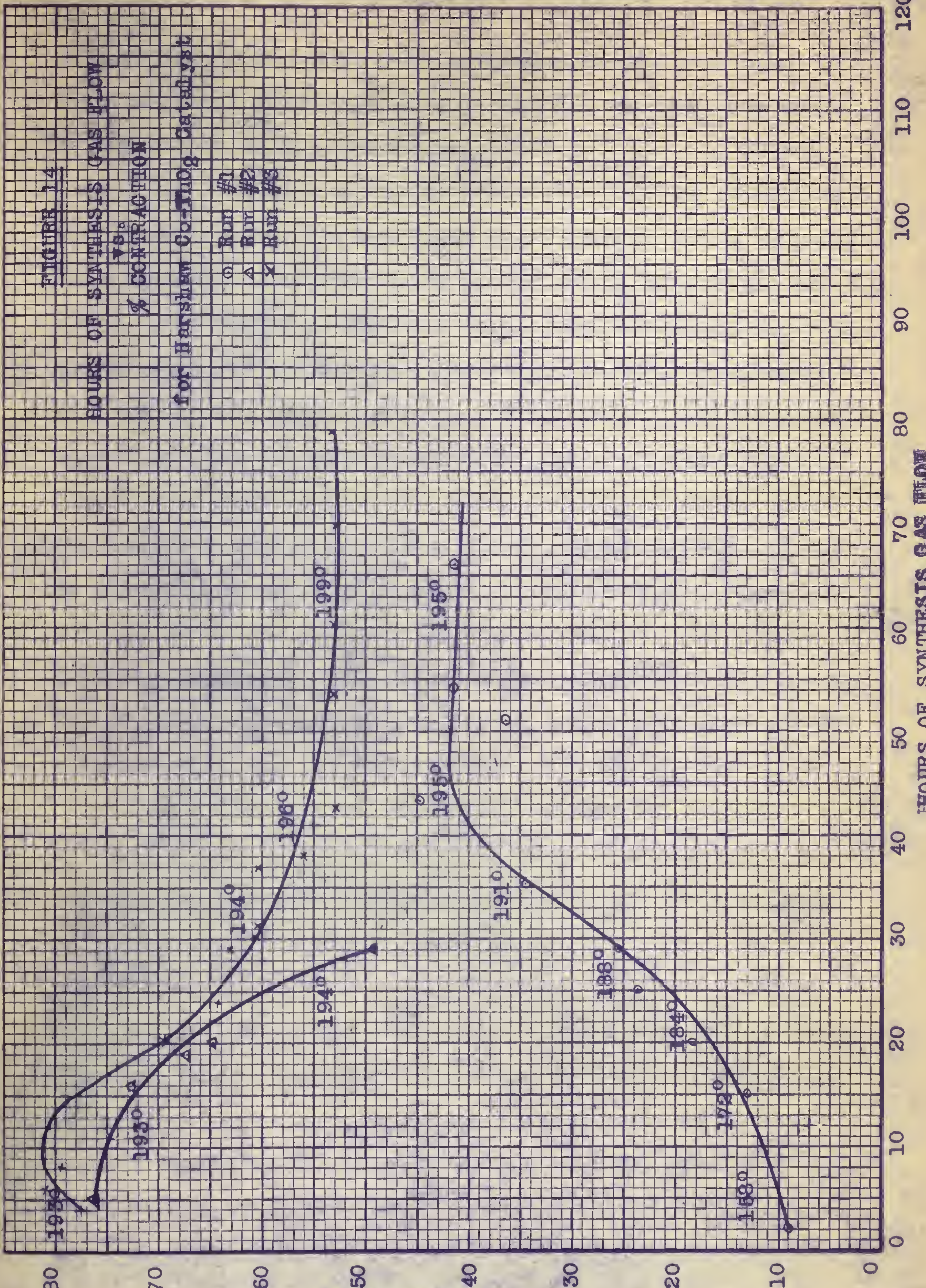

FIGURE 14

HOURS OF SYNTHESIS GAS FLOW vs. % CONTRACTION for Harshaw Co-ThO$_2$ Catalyst

contraction values after two or three days run were very close together for the different runs if the operating temperatures were at all comparable.

A range of temperatures from 172° to 190°C. has been used to enter the synthesis gas following a low temperature activation. Run #3 where the entering temperature was 156°C. gave better performance than run #2 where the entering temperature was 132°C. The advantage, however, of entering at a relatively low temperature and increasing this variable very slowly may be shown in run #4. Using this procedure a run of one hundred and twenty-three hours was made in which the end temperature was 203°C. and the final contraction was 64 per cent. The yield of solid and liquid hydrocarbons per cubic meter of synthesis gas for this long run was greater than for the shorter run #6, and almost as great as the yield for #5 run where two low temperature activations were carried out.

The various treatments carried out on this catalyst failed to bring the yield of solid and liquid hydrocarbons per cubic meter of synthesis gas above a level of approximately 45 grams per cubic meter, unless a short period of operation was used. This would tend to indicate that the maximum yields were being obtained from this catalyst. However, this is difficult to confirm since this Harshaw catalyst was not manufactured specifically for the Fischer-Tropsch synthesis of hydrocarbons, and no other data on this catalyst are available for comparison. Should the yields from other catalysts which were tested under similar conditions

be improved, another test on this Harshaw cobalt-thoria catalyst might be warranted.

Cobalt-Thoria-Magnesia-Kieselguhr Catalyst

Source - prepared by the U. S. Bureau of Mines

Weight used - 55.0 grams.

The test on this catalyst was made mainly to determine the benefits of the long reduction method employed. If the yields obtained were comparable to those stated by the Bureau of Mines then the procedure would be justified. However, not only was the reduction and conditioning procedure of the catalyst altered from that specified by the Bureau of Mines but also the operating pressure. Hence, for this type of test to be of any value, the catalyst should be reduced and tested according to the Bureau of Mines procedure, and then tested again using the long reduction and conditioning treatment and operated subsequently at atmospheric pressure.

The results obtained by the method of long reduction, conditioning and medium pressure operation are tabulated in tables #29, 30 and 31.

Table 29

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Conv. Range %	Starting Temp.	Conv. %
1	115.5	Long reduction	373			
		Conditioning	141-170	66-84		
		Operation @100 psi.	170-190	84-80-85		
			190-200	85-81-82		
		Low temp. act.	216			
		Operation	192-205	76-[illegible]-60	195	
		Low temp. act.	216			
2	84.0	Operation @ atm. press.	175-184	30	175	31
		Operation @ 100 psi.	184-205	30-78		

Table 30

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.19	57.30	29.43	0.00	1.71	12.50
	X 0.00	44.30	5.50	31.10	2.00	16.42
	0.00	39.90	22.00	5.55	11.92	14.95
2	0.12	43.00	27.10	16.05	6.10	6.92

X Immediately after a low temperature activation

Table 31

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m. Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	% Conversion to Cond.Hyd.
1	12.40	44.50	56.90	20.10	163.3	27.2
2	11.40	33.10	44.50	15.00	140.0	21.3

Discussion

Table 29 shows that this catalyst was given the long reduction and conditioning in the same manner as the previous catalysts. Operation was carried out at 100 psi. It is interesting to note that very high contractions (94%) were obtained during the conditioning (run #1, table 29) and that as soon as pressure was applied these contractions rapidly dropped to 60%. This is shown very clearly by the conditioning and operation curves (Figure 15). The temperature was raised from 170-190°C. at this time and contractions rose from 60% to 95%. The temperature was raised to 200°C. in an effort to maintain this contraction but it dropped to 60%, subsequently rising to 90%. Thus a low temperature activation was given the catalyst and the contractions rose to almost 90%, but dropped to 60% in a relatively short time. It was concluded that the catalyst could not be operated suitably at 100 psi., and hence run #2 (table 29) was initially carried out at atmospheric pressure. Only very low contractions were obtained (30%) and there was a considerable pressure drop across the converter, making flow control difficult. It was found necessary to commence operation at 100 psi. to overcome this pressure drop. Contractions then

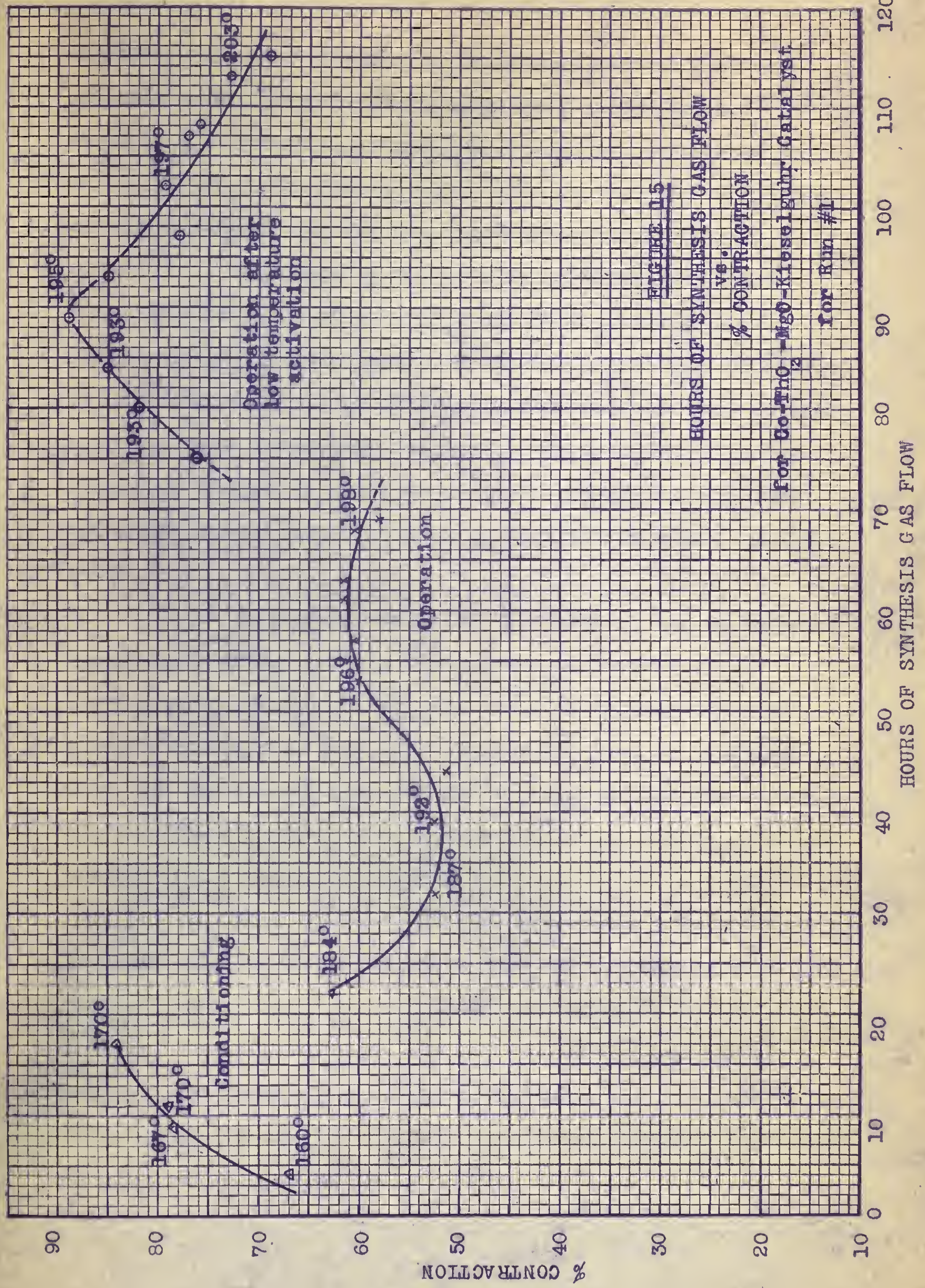

FIGURE 15

HOURS OF SYNTHESIS GAS FLOW
vs.
% CONTRACTION

For Co-ThO$_2$-MgO-Kieselguhr Catalyst
for Run #1

rose to 78%. The catalyst pellets when removed from the converter were found to be broken down, probably as a result of pressure operation. The catalyst was tested for a total of 190 hours during which time the catalyst was given a long reduction and two low temperature activations.

Considering the conditions under which the catalyst was operated, the yield of 56.90 grams of liquid hydrocarbons per cubic meter of synthesis gas (run #1, table 31) was reasonable. If an atmospheric pressure test on this catalyst gave comparable results to those obtained by the Bureau of Mines, it would confirm the reduction procedure and operational technique used in most of the other catalyst tests.

In run #1 (table 30) the residue gas analysis immediately after the low temperature activation is of considerable interest. The gas contains an exceptionally large percentage of methane. This would seem to indicate that the low temperature activation exposes much bare metal surface, where hydrogen can be chemisorbed to desorb methylene groups before they have polymerized.

This catalyst has not been given a conclusive test, and further tests should be carried out before any definite conclusions can be drawn. It seems evident, however, that the catalyst has not sufficient mechanical strength to withstand pressure operation. The irregular behavior of the catalyst under atmospheric pressure operation was due to collapse of the catalyst.

Cobalt-Manganese-Kieselguhr Catalyst

Source - prepared at the University of Alberta
by the authors

Weight used - 44.7 grams.

The data obtained for this catalyst is summarized in tables #32, 33 and 34. This is the first time that a cobalt catalyst promoted by manganese has been tested at the University of Alberta.

Table 32

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Starting Cont.%
1	111.5	Short reduction	370			
		Conditioning	182-195	7-35-15		
2	78.75	Long reduction	376			
		Conditioning	187-200	4-30-18		
		Low temp. act.	205			
3	100.5	Operation	190-198	76-34	190	
		Low Temp. act.	210			
4	51.75	Operation	190-200	64-34-40	184	50

Table 33

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.00	67.40	24.40	trace	trace	8.20
3	1.10	55.90	26.10	12.60	—	4.30
4	0.06	56.70	19.55	13.70	1.23	8.15

Table 34

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m. Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	% Conversion to Cond.Hyd.
1	—	—	—	6.45	13.40	—
2	0.50	1.23	1.73	10.56	[illegible].70	0.8
3	10.72	22.70	33.42	6.42	109.2	16.0
4	—	—	—	12.53	70.70	—

Discussion

From table 33 it can be seen that the conditioning after the short reduction of the catalyst resulted in very small contractions. Table 34 shows that water was the only liquid product produced during this time. The contractions rose to a maxima of 37% but dropped off to 15%. Even after the long reduction the conditioning resulted in insignificant hydrocarbon yields. The temperature was raised to 300°C. during the conditioning in an endeavor to obtain increased contractions, but the maximum contraction obtained was only 30%. A subsequent low temperature activation resulted in initially high contractions and an enhanced hydrocarbon yield, but these also dropped off rapidly. From the operating curve (Figure 16) this rapid decrease of contraction can be observed. The conditioning curve (Figure 16) indicates that the catalyst was not very active since only a contraction of 30% could be obtained, and this could not be maintained for any length of time. Further operation (run #4) resulted in a contraction increase from 64% to

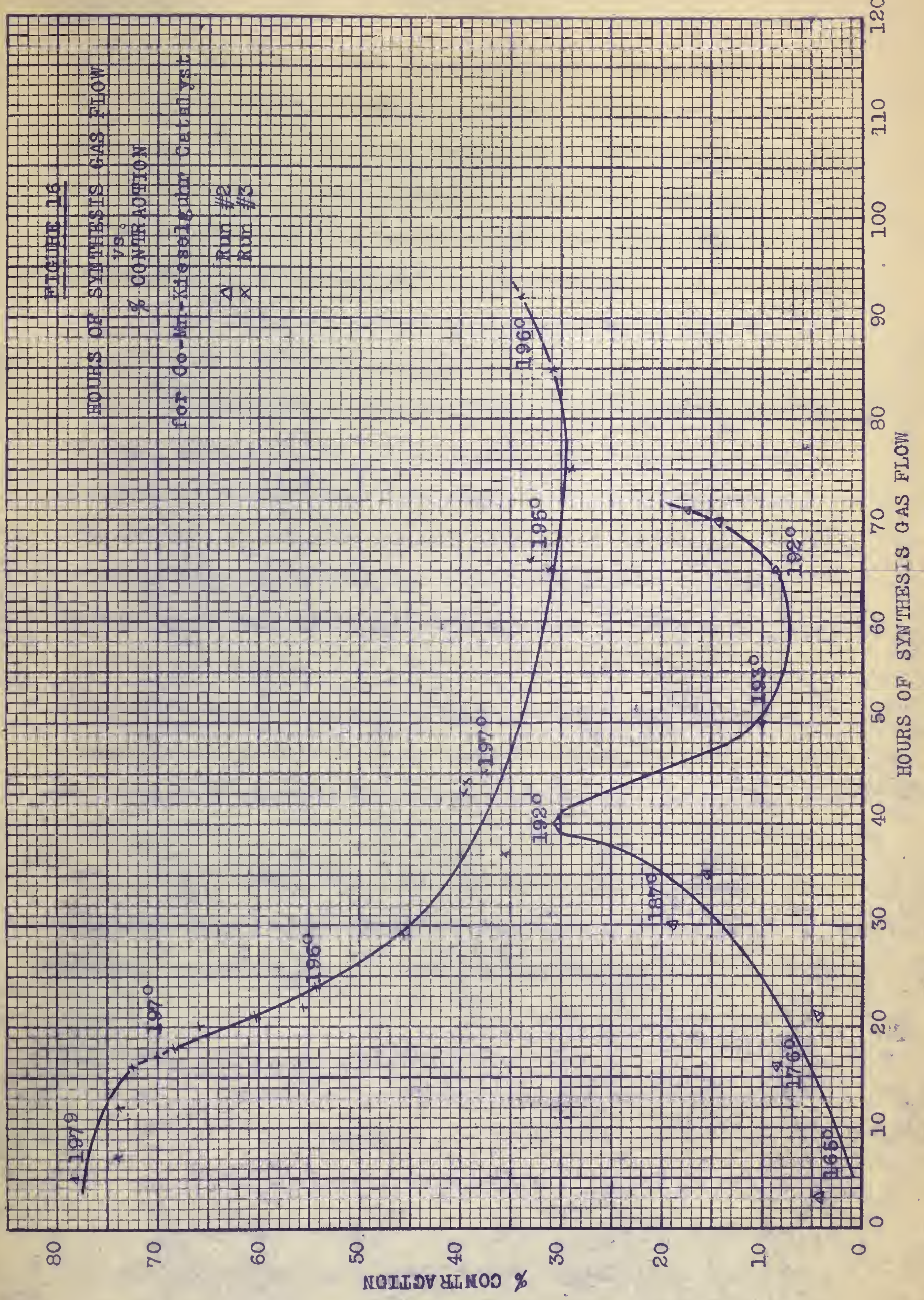

FIGURE 16

HOURS OF SYNTHESIS GAS FLOW
vs.
% CONTRACTION

for Co-Mn-Kieselguhr Catalyst

to 64% as the temperature was raised from 190 to 200°C, but this dropped off rather rapidly to 40%. The catalyst was discarded after these tests, during which operation was carried out on the catalyst for a total of 340 hours. In all, a short reduction, a long reduction and two low temperature activations were carried out on the catalyst.

From the preceding observations it can be assumed that the Co-Mn catalyst is not a very active preparation. If synthesis of liquid hydrocarbons occurs, it does so almost entirely in the period immediately following a low temperature activation. This may mean that active carbide centres on the catalyst surface are few in number and can be rendered relatively inactive after a very short synthesis period. The relatively large percentage of methane in the residue gas (12.50%, table 38, run #3) bears out the fact that there are probably few active carbidic centres and a large number of bare metallic centres, allowing rapid desorption of short chain gaseous hydrocarbons by chemisorbed hydrogen.

On the whole, this catalyst gave unsatisfactory results, and it is doubtful whether manganese alone is a suitable promoter for a cobalt base catalyst.

Nickel-Manganese Catalyst (Harshaw)

Source - Harshaw Chemical Company, Cleveland,
Ohio

Weight used - 54.9 grams.

The composition of this catalyst is unknown. The catalyst is not specifically a Fischer-Tropsch catalyst.

A summary of the results follows in tables 35, 36 and 37.

Table 35

History of Catalyst

Run No.	Hrs. Syn. Gas Flow	Treatment	Temp. °C.	Cont. Range %	Starting Temp.	Cont.%
1	68.0	Long reduction	376			
		Conditioning	188-197	18-75		
		Low temp. act.	205			
2	115.5	Operation	190-201	57-65	190	
3	74.0	Short reduction	302			
		Conditioning	185-200	10-16-40		
		Low temp. act.	210			
4	30.0	Operation	200-212	30-17	176	

Table 36

Residue Gas Analyses - Volume %

Run No.	Average Gas Analysis - Volume %					
	CO_2	H_2	CO	CH_4	C_2H_6	N_2
1	0.12	47.65	27.50	10.75	5.93	8.05
2	0.06	54.66	30.42	6.29	4.44	4.31
3	0.00	57.10	29.75	0.00	7.75	4.58

Table 37

Yields - Gms./cu.m. of Synthesis Gas Flow

Run No.	Yields - Gms./cu.m.					% Conversion to Cond. Hyd.
	Light Fraction	Heavy Fraction	Total Yield Cond. Hyd.	CO_2	H_2O	
1	5.17	18.58	23.75	20.60	105.0	11.4
2	4.35	3.03	7.38	5.63	86.25	3.5
3	5.90	2.42	8.32	14.34	90.90	4.0
4	0.35	——	0.35	18.70	55.70	——

Discussion

This catalyst was given the long reduction treatment and was subsequently given two low temperature activations and a short reduction. From the conditioning curve (Figure 17) it is evident that high contractions were obtained during the conditioning on run #1. The minima in this curve would probably not have arisen had the temperature been raised from 187 to 194°C. sooner than it was. The dotted curve indicates the possible shape of the contraction curve had this procedure been carried out. The highest yield was obtained from this catalyst during conditioning (table 57) and subsequently the activity of the catalyst dropped off so that very small yields were obtained. It is evident from run #3 that further operation after a low temperature activation did not result in contractions as high as those during conditioning, and yields of liquid hydrocarbons were small. A short reduction for four hours at 382°C. was given the catalyst in an endeavor to reactivate it. However, large contractions could not be regained. Subsequent operation after a low temperature activation resulted in extremely small contractions which continued to decline, although the operating temperature was increased to 212°C. Therefore the catalyst was discarded. The catalyst was tested for a total of 292 hours.

The small yield of liquid hydrocarbons might be due to the strongly hydrogenating characteristics of the catalyst and its lack of polymerization ability. It may, on the other hand, be due to the rapid deactivation of the

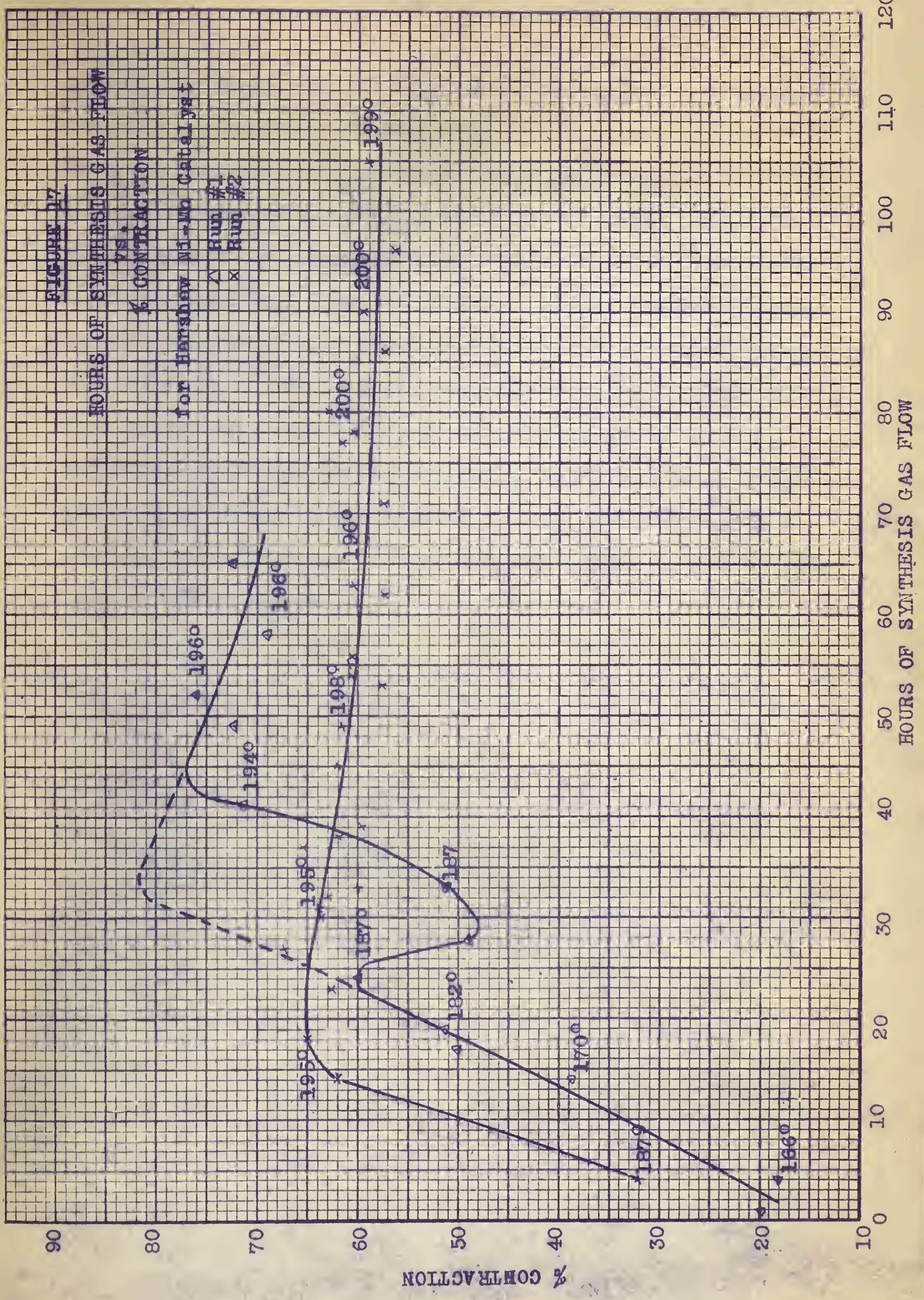

FIGURE 17

HOURS OF SYNTHESIS GAS FLOW
vs.
% CONTRACTION

for Harshaw Ni-Mo Catalyst

△ Run #1
× Run #2

active centres which are responsible for liquid hydrocarbon synthesis, possibly by being covered with heavy waxes. From the relatively increasing yields of the light fraction during successive operation, (table 37) it would seem that, when the catalyst is in an active state, heavier liquid and solid hydrocarbons form and probably hinder the subsequent synthesis, so that very large yields are not obtained throughout the test. Another explanation of reduced activity is the loss of active centres through volatilization of nickel carbonyls, which are highly volatile. With continued operation the catalyst is deactivated in such a way that its polymerization ability is affected, resulting in short chain hydrocarbon formation.

GENERAL DISCUSSION

Iron Catalysts

Neither the iron catalyst or the iron-copper catalysts have given encouraging results. With the former this is particularly true. Although the yields obtained with the iron-copper catalysts are nearly four times those for the iron catalyst, much improvement is necessary in both cases to duplicate published results (63).

An iron-copper catalyst from the same batch as catalyst #1 was tested previously (12). At that time a maximum yield of 14 grams per cubic meter of synthesis gas resulted, which is lower but of the same order as the yields obtained in the present investigation. Similarly, an iron catalyst tested previously (12) gave a maximum yield comparable to that obtained from catalyst #1, described above.

The amounts of carbon dioxide yielded by each catalyst appear excessive. This would seem to indicate that a preferential reaction other than the formation of liquid and solid hydrocarbons was taking place.

It is the authors' opinion that the testing of iron catalysts, or iron based catalysts, is unsatisfactory using the excessive amounts of hydrogen present in a $2H_2:1CO$ synthesis gas. This line of reasoning would conform to the facts stated by Fischer (35) regarding the presence of diluents in the synthesis gas.

Cobalt Catalysts

Three catalysts having the composition

Co-ThO$_2$-Kieselguhr were tested, that is cobalt-thoria #1, 2 and 3. Although the same procedure was used in every case during the catalyst preparation, better experimental control was achieved in the case of #2 than for the others. The effect of this is shown by the fact that catalyst #2 maintained a slightly higher contraction for longer periods of time than did either of the other two. It did not give higher yields of hydrocarbons, but this may be explained by the alkaline nature of this catalyst.

From the data, certain generalized conclusions may be drawn regarding cobalt-thoria catalysis. The main oxygen product from the synthesis was water, with minor amounts of carbon dioxide being produced. This agrees with the behavior of cobalt catalysts tested by other workers (6). The optimum maximum operating temperature has been placed at 200°C. in general practice. Although operation on these catalysts was occasionally carried out above this temperature, no advantage was gained, and in some cases poorer performance resulted. It would appear from the results obtained that a temperature of 198°C. is a satisfactory maximum.

Tests conducted by the authors would indicate that these cobalt catalysts require a fairly strenuous reduction to insure a reasonable activity. Increasing the reduction time, and lowering the initial conditioning temperature, had the effect of doubling yields, but there is no assurance that an even longer reduction might not increase yields to a still larger amount. The results obtained here definitely indicate the value of a long reduction period.

This is to be expected, since any large amount of oxides present in the catalyst would probably inhibit the formation of carbides, and thus have a deactivating effect on the catalyst with a corresponding hindrance in the synthesis reaction.

The exact composition of the Harshaw cobalt-thoria catalyst is unknown, and hence correlation of results is difficult. However, from the yields, nature of the product and general behavior, this catalyst apparently has a composition very similar to the other cobalt-thoria-kieselguhr catalysts.

From results obtained with the cobalt-manganese-kieselguhr catalyst, and also with the nickel-manganese preparation, the action of manganese alone as a promoter for this synthesis has not been encouraging. Both catalysts gave very poor performances, the nickel catalyst in particular giving very small yields. Nickel as a Fischer-Tropsch catalyst has not been found satisfactory by other workers (8) except over short periods, and the results obtained here confirm this observation. This has been explained by the special properties of nickel carbides and carbonyls, as has been previously discussed.

Some mention should be made of the cobalt-thoria-magnesia-kieselguhr catalyst. Insufficient tests were carried out to obtain conclusive results, but preliminary data indicate a considerably greater activity than any other catalyst tested.

An interesting observation was made regarding the cobalt catalysts. The pellets of cobalt-thoria

catalyst #1 were apparently somewhat less dense than those for #2 and 3 cobalt catalysts. A considerably smaller weight of this catalyst gave as high yields and as good general performance as heavier pellets of the same composition for the other catalysts. Hence, it is possible that there is a relationship between the relative densities of the pellets and the active surface area in the reduced form. This is something which may be investigated in static adsorption studies on the freshly activated catalyst.

Product Analysis

Table 30 provides a summary of the results of the analyses carried out on the products. This work was carried out by an undergraduate student (65a) using the total product produced from the specific catalysts. The yields from any catalyst were not further subdivided from the two cuts, a high boiling fraction from the steam pot and a low boiling portion from the water-cooled pot. In many instances the high boiling point fraction consisted almost entirely of waxes, solid at room temperature. Hence, certain tests performed on the low boiling fraction were not possible with this high boiling fraction. A large portion of the water produced in the synthesis condensed in the catchpot with the high boiling point hydrocarbon, a small amount passing over with the lighter fraction to the second catchpot. For testing purposes the water from both of these sources was analysed separately.

Figures 18, 19 and 20 show the distillation

Table 33

Analysis of Synthesis Products

Catalyst	Fraction	Hydrocarbon Layer			Water Layer			
		Density 20°/4°	Refractive Index	Aniline Point	Density 25°/25°	% Boiling below 100°C.	Qualitative Tests: Alcohols	Qualitative Tests: Aldehydes & Ketones
Co-ThO$_2$ #1	Heavy	0.704	Wax	89.4	0.9962	Trace	Strong	Weak
	Light	0.7060	1.4040	74.8	0.9700	8	Strong	Neg.
Co-ThO$_2$ #2	Heavy	—	Wax	94.0	0.9957	Trace	Strong	Weak
	Light	0.7088	1.4004	73.6	0.9951	2.7	Strong	Weak
Co-ThO$_2$ #3	Heavy	0.744	Wax	96.6	0.9969	Trace	Strong	Weak
	Light	0.6961	1.4035	70.0	0.9888	8.6	Strong	Neg.
Co-ThO$_2$ (Harshaw)	Heavy	0.741	Wax	95.1	0.9904	Trace	Strong	Weak
	Light	0.6985	1.3999	70.5	0.9913	6-7	Strong	Weak
Co-ThO$_2$-MgO	Heavy	0.7385	1.4514	82.2	0.9961	1.3	Strong	Neg.
	Light	0.6740	1.3932	61.2	0.9945	6	Strong	Neg.
Co-Mn	Heavy	0.715	Wax	94.5	0.9966	Trace	Strong	Weak
	Light	0.7143	1.4078	75.7	0.9943	5	Strong	Neg.
Ni-Mn (Harshaw)	Heavy	0.800	1.5240	43.9	1.0005	Trace	Weak	Weak
	Light	0.746	1.4119	79.3	0.9929	5.0	Strong	Neg.
Fe #3	Heavy	X	X	X	X	X	X	X
	Light	0.7427	1.4000	75.8	0.9764	20	Strong	Weak
Fe-Cu #2	Heavy	0.7935	1.4317	70.5	1.0155	X	Strong	Neg.
	Light	0.7300	1.4246	45.1	0.9736	36	Strong	Weak

X not sufficient product

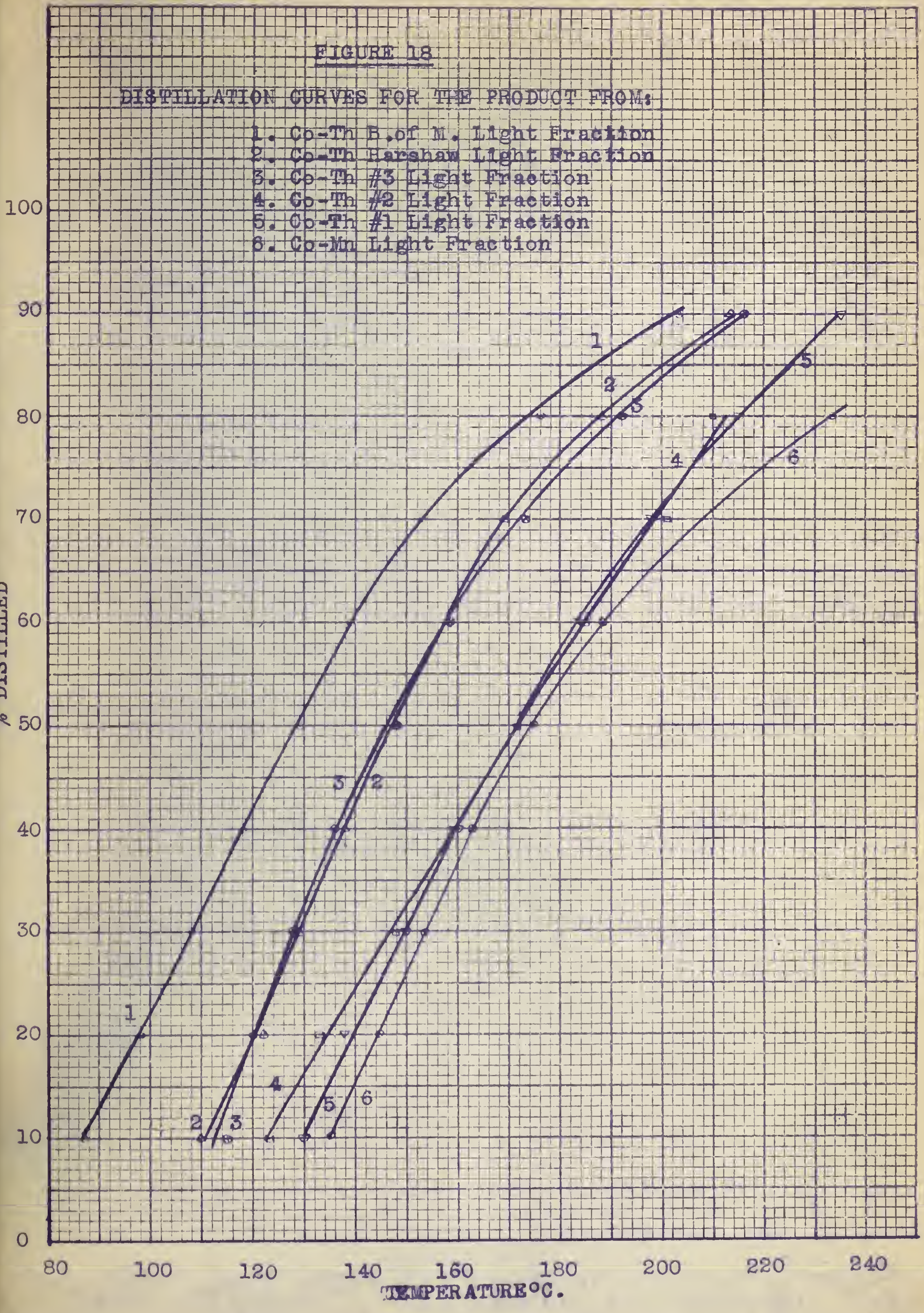

FIGURE 18

DISTILLATION CURVES FOR THE PRODUCT FROM:

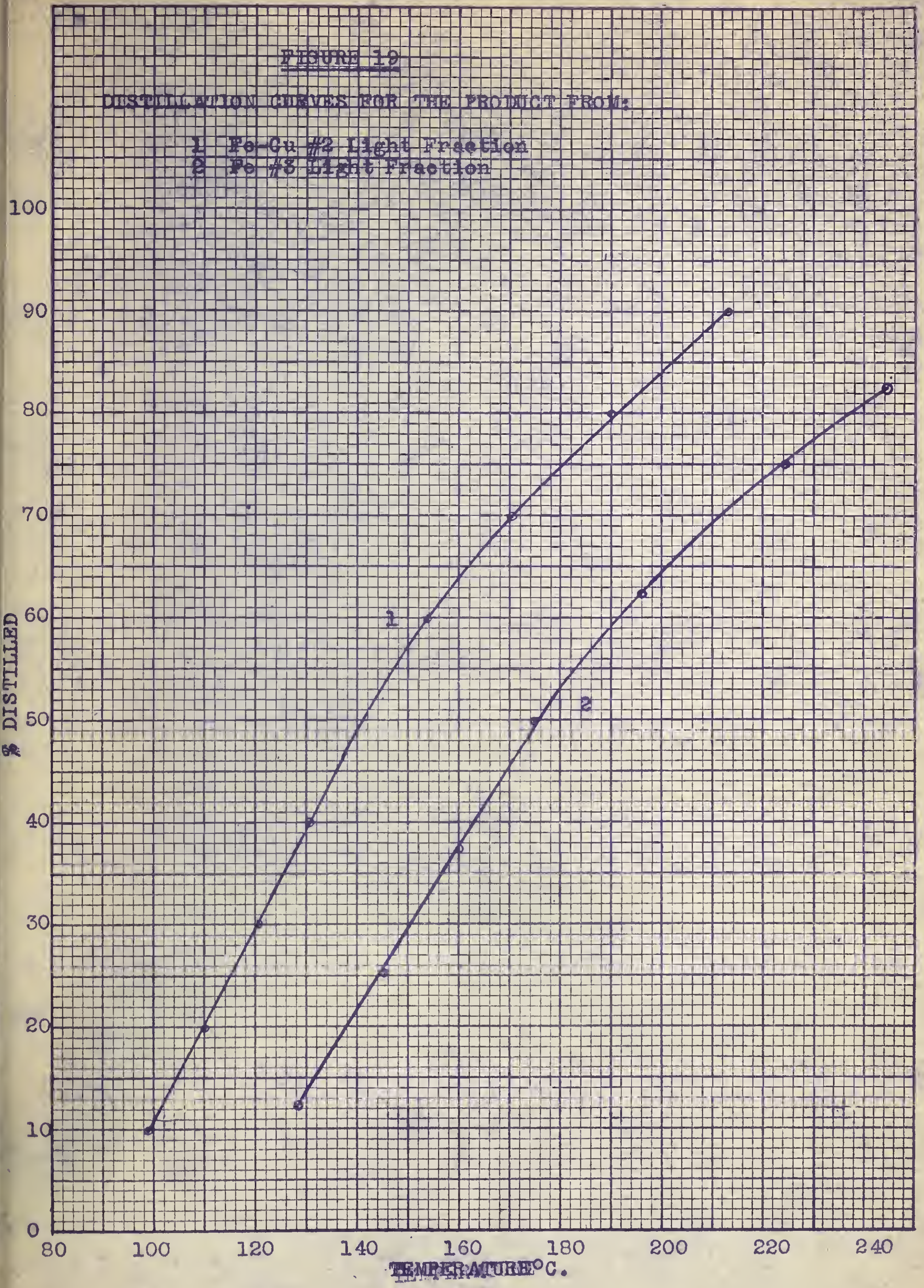

FIGURE 19

DISTILLATION CURVES FOR THE PRODUCT FROM:

1 Fe-Cu #2 Light Fraction
2 Fe #3 Light Fraction

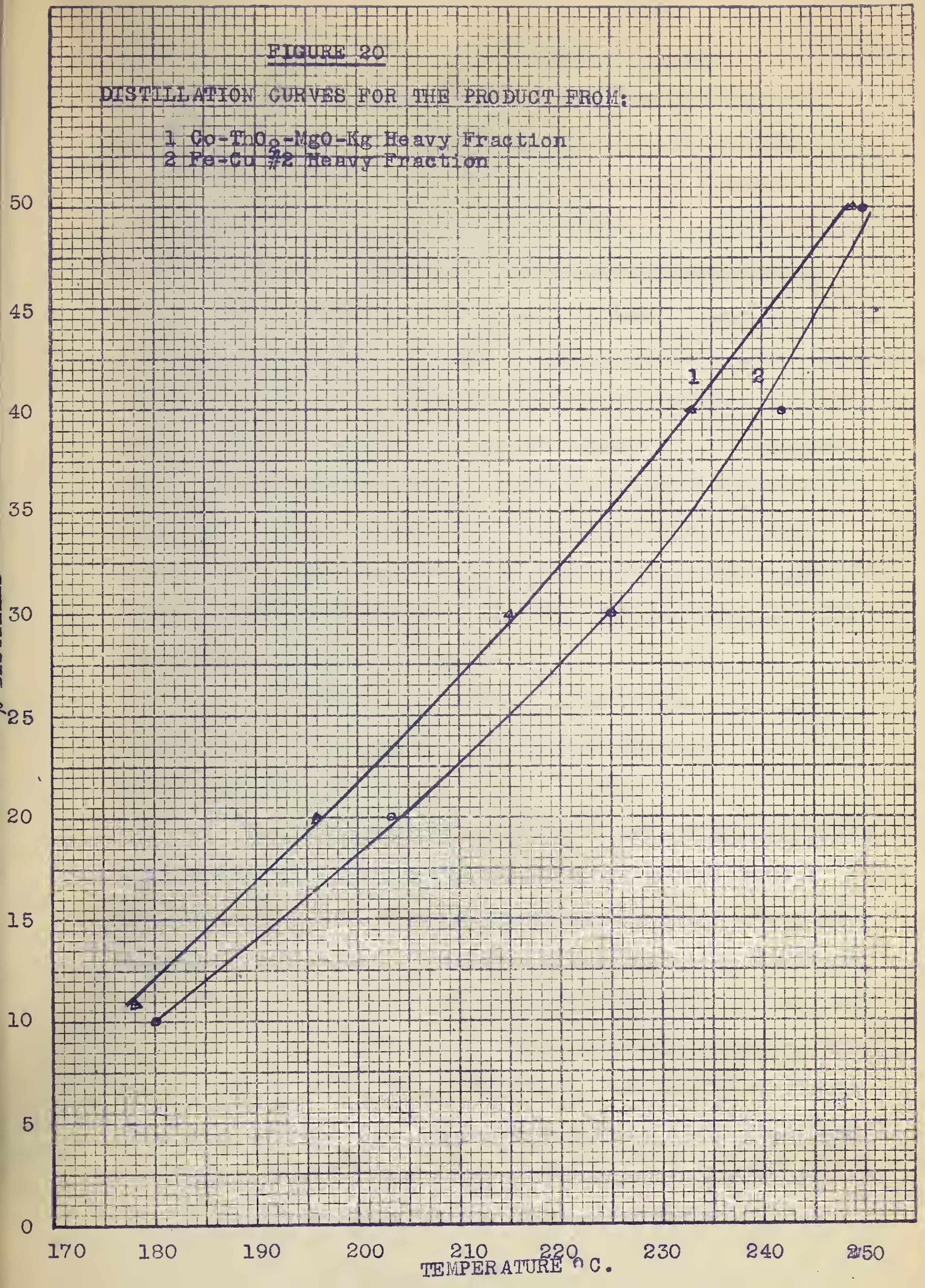

FIGURE 20

DISTILLATION CURVES FOR THE PRODUCT FROM:

curves obtained for the product, where sufficient amounts were available. In general it was not possible to carry out distillation on the high boiling point fractions since these products were mainly wax. Two distillations were run, however, on two high boiling point fractions. In these the distillation was stopped at 250°C. since any wax present would tend to plug the condenser. No data on initial boiling points are available. In the distillation of the low boiling point fraction the temperatures were not allowed to exceed 250°C. This was done to prevent cracking of the residue, since it was necessary to use the distillate for chemical analyses. It will be noted that the low boiling point fraction from both the iron based and cobalt based catalysts is composed of hydrocarbons of which approximately 20% boil outside the gasoline range.

Table 32 indicates the densities, refractive indices and aniline points obtained on the light and heavy hydrocarbon fraction.

All cobalt catalysts with the exception of the cobalt-thoria-magnesia catalyst produced a high boiling fraction which was a suspension of wax in heavy hydrocarbon oil. The average density of the light and heavy fraction obtained from the latter catalyst is 0.73, which is very close to the value 0.75 given by the United States Bureau of Mines. The densities of all light fractions from cobalt catalysts were unexpectedly low. Both the heavy and light fractions from the iron and iron-copper catalysts were liquids, and had a considerably greater density than corresponding fractions

from cobalt catalysts.

The refractive indices check well with those obtained previously for similar catalysts (12).

The heavy fractions, in all but one instance, had higher aniline points, thus roughly indicating that the high boiling fraction is more saturated than the low boiling fraction. The product from the cobalt-thoria-magnesia catalyst gave the lowest aniline points. The product from the iron catalyst was considerably more unsaturated than that obtained from any cobalt catalyst. This is in accordance with existing experimental facts (6). The iron-copper catalyst produced a light fraction which was far more unsaturated than that from the iron catalyst.

Quantitative tests to determine the amounts of olefins present in the product were done in two cases where sufficient product was available. A number of high boiling point fractions from tests on cobalt catalysts were mixed, and the resulting mixture was analysed for olefin content. The method of analysis consisted of agitating the hydrocarbons with concentrated sulphuric acid and washing out the sludge so produced. Results indicate that the fraction had an olefin content of approximately 25% by volume. Hence it may be assumed from aniline point data that the low boiling fractions contain an olefin content in excess of 25%. A similar test on a combined low boiling fraction produced when using iron and iron-copper catalysts indicated very high olefin content, probably in excess of 50 percent.

Saponification numbers carried out individually

on the hydrocarbon products from all the catalysts indicate minute amounts of esters or acids. The pleasant aroma of the products also is indicative of traces of esters.

A summary of the data from the analyses of the water produced in the syntheses is also given in table 32. From the densities of the heavy fractions it is apparent that there are present very small amounts of water soluble material. This is verified by the amounts of material boiling below 94°C. In the water removed along with the low boiling hydrocarbon fraction, however, much larger amounts of water soluble materials were found. This is paralleled by the correspondingly lower densities. This effect is particularly noticeable with the iron and the iron-copper catalysts, where there was present in the water product 20 and 28% respectively of material boiling below 94°C.

The qualitative tests for alcohols, aldehydes and ketones indicate the predominant presence of alcohols with only minor amounts of aldehydes and ketones. It can be assumed that the water soluble material was mainly alcohols. This conforms with information obtained on commercial operation (64).

GENERAL SUMMARY

Ten catalysts have been tested for their ability to promote the Fischer-Tropsch synthesis. The results obtained have been presented together with discussions of the performance and characteristics of each catalyst. None of the catalysts has achieved the desired results, but some definite advances have been made.

Catalysts, which had previously given unsatisfactory results, (12) showed a considerable improvement in yields when tested a second time using a different reduction procedure and a modified conditioning technique. The catalysts prepared by the authors and tested in the same manner did not show a significant improvement in behavior over those previously prepared (66a), although during the preparation a more accurate control of the various steps was maintained. In general, the cobalt base catalysts were found to give a much better performance than the iron catalysts.

The products obtained varied considerably. The cobalt catalysts prepared at the University of Alberta gave a large proportion of solid waxes, whereas the cobalt catalyst prepared by the U. S. Bureau of Mines gave a product which was entirely liquid. The iron catalyst yielded mainly liquid products. All the products contained a good percentage of unsaturated material, with the iron catalyst yielding notably large amounts. Tests carried out for the detection of low boiling, water soluble organic compounds gave some interesting results. Nearly all the catalysts produced some of these compounds, largely alcohols, with the iron catalysts

yielding an amount up to 50% by volume of the water layer, a lesser proportion being obtained from the cobalt catalysts. However, it should be borne in mind that the cobalt preparations produced a much greater volume of water layer than the iron catalysts.

Although better success was attained than in previous catalyst testing with this apparatus, a satisfactory catalyst has not yet been found. The inconclusive tests on the U. S. Bureau of Mines catalyst indicate that this preparation would probably give high yields if tested at atmospheric pressure. If this is the case, then it would appear that the modified reduction method and operational procedure adopted by the authors was adequate, and the failure of the other catalysts was due to the nature of the material itself. The answer may be found by the addition of magnesium oxide as a promoter, or in an even more careful catalyst preparation. The properties of surface area (i.e. pellet size) and density of the catalyst pellets might also prove to be a factor influencing catalyst behavior.

On the other hand, should the U. S. Bureau of Mines catalyst fail to give the desired results, then new variations in reduction and activation techniques are indicated. It is possible also that more accurate control in the step-wise conditioning procedure might prove beneficial. No evidence of catalyst poisoning has been obtained from sensitive tests which have been carried out. This is felt to be the least likely explanation of the observed catalyst behavior.

The poor results obtained from the iron catalysts tested may be largely due to the hydrogen:carbon monoxide ratio of the synthesis gas. In order to obtain conclusive results on these catalysts a synthesis gas with a 1:1 ratio of hydrogen:carbon monoxide should be used.

In general, no difficulty was experienced in maintaining steady operating conditions and collecting reliable data during tests.

APPENDIX A

Sample Calculation of Material Balance

A sample material balance is calculated below. Such a calculation serves as an indication of the accuracy of the data collected and the degree of control which has been maintained during operation. Certain assumptions have also been made for the purpose of simplifying the calculation of results, and a material balance forms an excellent check on the validity of such a procedure.

The data used is that obtained during run #6 on the cobalt-thoria-kieselguhr catalyst #3.

Gas density data ([illegible])

	760 mm and 0°C.	700 mm and 24°C.
CO_2	1.977	1.662
H_2	0.0898	0.0756
CO	1.250	1.051
CH_4	0.717	0.603
C_2H_6	1.357	1.140
N_2	1.251	1.052

The densities at 700 mm and 24°C. were calculated by assuming that the perfect gas law holds for these conditions.

Gas in from inlet flowmeter readings = 603.0 litres

Gas out from outlet gasmeter readings = 253.0 litres.

Since the average composition of the outlet gas is known, the weight of the off-gas can be calculated.

	Av. Comp. %	Density grams/lit.	Weight grams
CO_2	0.21	1.088	0.90
H_2	53.00	0.0755	10.43
CO	31.10	1.061	34.40
CH_4	5.40	0.603	0.92
C_2H_6	3.12	1.140	0.19
N_2	6.49	1.062	17.62
	100.00		151.04

Weight of product obtained = 21.46 grams

Weight of carbon dioxide produced = 10.39 grams

Weight of water produced = 75.00 grams (1 cc. water = 1 gm.)

Then weight of total products after synthesis = 238.27 grams.

A feed gas analysis made during this run showed a hydrogen:carbon monoxide ratio of 2.04:1, with less than 0% of other materials being present.

If it is assumed that only carbon monoxide and hydrogen are present and the inlet gas temperature is 24°C. i.e. room temperature, then the gas density can be calculated.

Density of inlet gas = $(\frac{2.04}{3.04} \times 0.0755) + (\frac{1}{3.04} \times 1.061) =$

0.3967 gms./litre

Weight of synthesis gas used = 603 × 0.3967 = 239.5 grams.

Then weight in = 239.5 gms. Weight out = 238.3 gms.

Percent error in this case = $\frac{1.2}{239} \times 100 = 0.50\%$

The data calculated in this example appears to be quite reliable as the result indicates. This is probably due to the fact that very steady operation was maintained during this particular run on this catalyst. Other runs,

for this and for other catalysts, during which such steady operation was not maintained, would, of course, show a greater error in the calculation of a material balance.

It is apparent, however, that when steady operation is achieved, reliable data is obtained, and such assumptions as have been made here cause no appreciable error in calculated results.

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B29752